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TABLE OF CONTENTS

INORGANIC SEMINAR ABSTRACTS

1968-1969

Page

COORDINATION NUMBER AND GEOMETRY OF SOME COPPER(II)
AMINE COMPLEXES -
Walter John Kasowski

1

SUBSTITUTION REACTIONS OF OCTAHEDRAL METAL CARBONYL COMPLEXES -
Richard L. Kieft

1

PRODUCTION AND STUDY OF TITANIUM MONOHALIDES BY FLASH HEATING -
Robert L. Diebner

2

THEORIES OF BONDING AND STRUCTURE IN TRANSITION METAL SYSTEMS -
John B. Callen

9

SOME MAGNETICALLY ANOMALOUS COMPOUNDS OF IRON(II) -
Lucille Novak

14

PROTONATION OF ORGANOMETALLIC TRANSITION METAL COMPLEXES -
David P. Novak

19

FIVE COORDINATE COMPLEXES OF DIVALENT COBALT -
Thomas Maier

22

COBALT-59 NUCLEAR QUADRUPOLE RESONANCE -
Raymond S. Stewart

25

STEREOCHEMICALLY NON-RIGID ORGANOMETALLIC MOLECULES -
R. Sneath

28

FLASH HEATING AS A TECHNIQUE FOR HIGH TEMPERATURE SPECTROSCOPY -
Michael Garrett

33

BIO-INORGANIC SYSTEMS: THE DETERMINATION OF THE CHEMICAL
AND STRUCTURAL PROPERTIES OF HEMOGLOBIN -
James S. Swanson

30

PHOTOCHEMISTRY OF Cr(III) AND Co(III) INORGANIC COMPLEXES -
Robert L. Chiang

33

INFRARED STUDIES OF THE TRANS INFLUENCE IN SQUARE
PLANAR COMPLEXES -
Mel Memering

38

STRUCTURAL STUDIES OF CHLORO AND AQUOCHLORO COMPLEXES OF
NICKEL(II) -
Fred Ross

41

SPIN DELOCALIZATION IN SIGMA SYSTEMS -
Roger Cramer

43

RELAXATION METHODS IN KINETIC STUDIES -
Kathy Myers

44

JUN 11 1969

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Table of Contents (continued)	Page
AN INVESTIGATION OF THE CHRONOPOTENTIOMETRIC OXIDATION OF Pt(II) - Sn(II) COMPLEXES - Denis F. DeCraene	48
NOBLE GAS CHEMISTRY - George F. McKnight	50
STUDIES OF THE EFFECTS OF FLASH HEATING ON CATALYTIC SURFACES - W. Ronald Cares	54
ION CYCLOTRON MULTIPLE RESONANCE AND ITS APPLICATION TO THE STUDY OF GAS-PHASE ION-MOLECULE REACTIONS - Eric F. Johnson	59
APPLICATIONS OF THE WOODWARD-HOFFMANN RULES TO TRANSITION METAL CATALYSIS - Joseph J. Brooks	62
NMR STUDY OF PENTAFLUOROPHENYL DERIVATIVES AND ITS APPLICATION TO THE STUDY OF CHEMICAL BONDING IN INORGANIC COMPOUNDS - Lim Yau-Yan	65
STRUCTURAL AND SPECTROSCOPIC STUDIES OF CERTAIN TRANSITION METAL HALIDES - Gary McPherson	69
STRUCTURAL STUDIES OF ORGANOMAGNESIUM COMPOUNDS - Joe D. Toney	71
STUDIES OF TRIETHYLENEDIAMINE COMPLEXES OF RUTHENIUM - Sister Helen Elsbernd	74

INFRARED STUDIES OF THE TRANS INFLUENCE IN SQUARE PLANAR COMPLEXES

Mel Memering

January 7, 1969

Introduction

In 1926, Chernyaev¹ invoked the term "trans effect" to describe the influence of a coordinated group (L) upon the ease of preparing complexes of platinum(II) in which the ligand trans to it in the square plane had been replaced. Several theories have been advanced in attempts to describe this phenomenon. Most early theories of the trans effect, notably the electrostatic polarization theory,² considered destabilization of the ground state, e.g., a weakening of the platinum-ligand bond trans to L. More recent explanations have emphasized the effect of L on the energy of the activated complex for both pi-^{3,4} and sigma-⁵ bonding trans directors.

The trans "influence"⁶ is distinct from the trans "effect" since it concerns the strength of the trans metal-ligand bond rather than the kinetic lability of the trans ligand. This seminar will be concerned with the use of infrared spectroscopy to measure the influence of ligands on other metal-ligand bond strengths in square planar complexes. The conclusions reached in these IR studies are based almost entirely on the assumption that relative frequencies roughly parallel force constants and in turn bond strengths.

Trans-Pt(NHR'R)LCl₂ complexes

NHR'R = NH₃, piperidine, toluidine, n-octylamine
L = neutral ligand

Chatt and his co-workers^{7,8} investigated the changes in the N-H stretching frequency in complexes of the type trans-Pt(NHR'R)LCl₂ as the ligand L was varied. A decrease in the N-H frequency indicates a weaker N-H bond which in turn indicates a shift of electron density from the nitrogen atom toward platinum and results in a strong Pt-N bond. Results indicate that there is essentially a linear relationship between ν N-H and electronegativities of the donor atoms of the L groups. It was also found that the order of Pt-N bond strength closely parallels the trans effect series. Because of a discrepancy in the relation between the frequency and intensity of the N-H bands, Chatt posited both a mesomeric and an inductive mechanism to explain the transmission of electronic effects across the platinum atom. It was further suggested that the N-hydrogen atom interacts in some way with the d-orbitals of platinum.

Powell⁹ thought it better to study the Pt-N stretch directly in a limited series of trans-Pt(NH₃)LCl₂ and obtained results similar to Chatt's.

Trans-PtL₂XR complexes

L = substituted phosphines or arsines

X = anionic ligands

R = H, CH₃, C₂H₅

Chatt et. al.^{8,10} measured the Pt-H stretching frequencies in a series of platinum hydrides of the type trans-PtL₂XH and found that their trans influence series corresponded exactly to the trans effect series. A cis influence was also noted.

The previous series was extended to a study of Pt-C stretching frequencies in the series trans-Pt(PR₃)₂XR (R = CH₃, C₂H₅).¹¹ With but one exception the same results were obtained as with the hydrides.

Cis- and trans-ML₂X₂ complexes

M = Pd, Pt

L = neutral ligands

X = halide

In studies of cis-complexes of this type, Chatt¹² and his co-workers noted that effects on the M-X bond are largely due to the different electronegativities of the donor atoms of the L groups. Durig et. al.¹³ reported similar investigations on a large number of analogous palladium complexes. These workers concluded that the trans influence for substituted amines is: RNH₂ > ArNH₂ > NH₃. The anomaly for pyridine was explained by pi-bonding. In both series, a small cis influence was noticed; the effect was more pronounced for palladium.

Cis- and trans-M(NH₂R)₂X₂ complexes

M = Pd, Pt

R = H, CH₃

In a detailed study, Nakamoto et. al.¹⁴ observed a trans and a slight cis influence on the Pt-N bond, both having the order: I⁻ > Br⁻ > Cl⁻. Similar results were obtained by Kharitonov et. al.¹⁵ on the bis-methylamines and by Durig et. al.¹⁶ on the palladium amines. Essentially the same results were obtained by Rosevear and Stone¹⁷ on the complexes cis- and trans-Pt(PEt₃)₂(C₆F₅)X where $\nu_{\text{Pt-P}}$ was used as the detector frequency.

Trans-PtC₂H₄(4-Z-py-O)Cl₂ complexes

4-Z-py-O = para substituted pyridine oxide

Orchin and his students¹⁸ have investigated the effect of various ligands trans to ethylene in a Pt(II) complex on the nature of the olefin-Pt bond. A plot of $\nu_{\text{C=C}}$ versus pK_a of the substituted pyridine oxide indicates that there is a linear decrease in $\nu_{\text{C=C}}$ with an increase in pK_a. This implies a strengthening of the Pt-C₂H₄ bond with increasing basicity of the trans ligand. However, subsequent literature tends to discredit this relationship.¹⁹

Conclusion

Infrared spectroscopy has been shown to be a useful and valid method to obtain an indirect measure of the influence of ligands on other metal-ligand bond strengths. It would be helpful if complete vibrational analyses were performed so that force constants may be compared rather than stretching frequencies especially in complexes involving pi-bonding

where coupling between modes may be more important. Furthermore, because of the lack of research on the directive influences in octahedral complexes,²⁰⁻²³ it would be worthwhile to investigate the relationships between the trans influence and the trans effect for these complexes also.

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STRUCTURAL STUDIES OF CHLORO AND AQUOCHLORO COMPLEXES OF NICKEL(II)

Fred. Ross

January 9, 1969

Introduction

Complexes formed by nickel(II) with chloro and aquo ligands were once believed to be few in number and simple in structure. More recently, however, X-ray investigations have shown that a number of complexes (many of unusual structure) can be stabilized. These compounds are most conveniently grouped according to their coordination geometry; complexes of tetrahedral, five-coordinate, and octahedral symmetry have now been characterized.

Compounds

Tetrahedral: Until recently, tetrahedral coordination for nickel(II) was considered rare¹ as late as 1962, $[\text{Ph}_4\text{As}][\text{NiCl}_4]$ was one of only a few compounds proven to contain tetrahedral nickel(II)² and was the only compound containing NiCl_4^{2-} which had been studied extensively. Although tetrahedral complexes are now becoming common for nickel, the NiCl_4^{2-} is still the only species reported for chloro or aquo ligands.

Five-Coordinate: No compounds containing only water molecules or chloride ions as ligands have been reported in the literature. In fact, very few compounds containing five-coordinate nickel(II) with mono-dentate, non- π -bonding ligands are known. Studies of lattice stabilization effects by Quagliano and Goedkin³ have led to the preparation of $\text{C}_7\text{H}_{15}\text{N}_2(\text{H}_2\text{O})\text{NiCl}_3$ and $[\text{C}_7\text{H}_{15}\text{N}_2]_2\text{NiCl}_3$, both of which contain five-coordinate nickel(II). The former complex has a "Zwitter ion" structure with $\text{C}_7\text{H}_{15}\text{N}_2^+$ acting as a cation and as a ligand. It possesses a geometry somewhat distorted from that of a trigonal bipyramid. The latter complex contains the unusual Ni_2Cl_3 anion which is a bridged, binuclear structure with distorted square pyramidal geometry about the nickel atom.

The spectra of these compounds can be suitably fitted to the energy level diagrams of Ciampolini,⁴ but assignments are ambiguous if the structure is not known.

Octahedral: Six coordination about the nickel atom is achieved in two extremes for compounds formed with these ligands.

1) In compounds of the formula MNiCl_3 , chains of octahedra sharing faces provide nickel atoms in sites of D_{3d} symmetry.⁵ These compounds are formed for numerous cations ($\text{M} = \text{Rb}^+$, Cs^+ , Tl^+ , Me_4N^+).

2) Compounds containing octahedral nickel(II) in the absence of bridging are relatively few in number. The hexaquaonickel(II) ion has been extensively studied,^{6,7} but is⁸ not found in hexaquaonickel(II) chloride. X-ray studies have shown⁹ that trans $\text{Ni}(\text{H}_2\text{O})_4\text{Cl}_2$ units and two lattice water molecules are present in this compound. The structure of the compound $\text{C}_6\text{H}_{14}\text{N}_2\text{NiCl}_4 \cdot 4\text{H}_2\text{O}$ has recently been found to contain the anion $\text{Ni}(\text{H}_2\text{O})_3\text{Cl}_3^-$ rather than the expected trans- $\text{Ni}(\text{H}_2\text{O})_2\text{Cl}_4^{2-}$ ion.

The spectra of these compounds are all closely similar to that expected for a true octahedral complex. Some small differences are observed, but much more study is necessary before it can be concluded that these differences are indicative of a specific coordination geometry.

Conclusions

The determination of the crystal structures of the compounds $C_7H_{15}N_2(H_2O)Cl_3$, $[C_6H_{16}N_2]_2Ni_2Cl_8$, and $C_6H_{14}N_2[Ni(H_2O)_3Cl_3]Cl \cdot H_2O$ were performed during this study and hydrogen bonding interactions are found to be important in all three. Extensive hydrogen bonding appears to be critical in stabilizing the $Ni_2Cl_8^{4-}$ anion as it cannot be prepared with a proton replacing the methyl group of the $H^+N(CH_2CH_2)_3N^+CH_3$ cation.

Analysis of the electronic absorption spectra recorded for each of these compounds leads to two conclusions. First, the energy level diagrams calculated for five-coordinate nickel(II) do not permit an unambiguous assignment of electronic spectra for these compounds, and second, octahedral complexes of nickel(II) with only aquo or chloro ligands differ only slightly in the character of their respective electronic absorption spectra and much caution is recommended in the analysis of these differences.

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SPIN DELOCALIZATION IN SIGMA SYSTEMS

Roger Cramer

February 11, 1969

In recent years there has been considerable interest in the field of NMR contact shifts. Considerable attention has been given to interpretation of contact shifts in terms of metal-ligand bonding. For example, LaMar proposed that the observed pi type shifts of the ring protons of $(\text{O}_3\text{P})_2\text{NiX}_2$ were produced by metal-ligand pi bonding.¹ Similar proposals were made to explain the contact shifts of $\text{Ni}(\text{C}_6\text{H}_5\text{CN})_6^{+2}$.² However, the observation of pi type shifts in the $\text{Ni}(\text{L})_6^{+2}$ complexes where L is benzylamine and analine cast doubt on the use of simple mechanisms to interpret contact shift data.³

We decided to prepare the complexes $\text{Ni}(\text{L})_6^{+2}$ where L is pyridine, 4 Me-pyridine, 3 Me-pyridine, and 4 vinylpyridine and attempt to determine the spin delocalization mechanism for these complexes. The NMR contact shifts for these complexes were determined by standard mole fraction techniques³ in propylene carbonate solution. The expected pattern of shifts for these complexes is an all sigma pattern. However, the fact that the methyl group of 4 Me-pyridine shifts up-field shows that there is some amount of pi spin delocalization in these complexes. In order to quantitatively determine the amount of sigma and pi delocalization in these complexes, we decided to carry out Extended Hückel molecular orbital calculations. In order to determine the ability of Extended Hückel calculations to reproduce electron-proton coupling constants, we first tried a series of organic sigma radicals.⁴ The results for these free radicals were favorable, so we then applied these calculations to the contact shift problem.

Extended Hückel molecular orbital calculations were carried out on the ligands in order to determine the coupling constants which would result if one unpaired electron were delocalized in each of several orbitals. The fraction of unpaired spin in each molecular orbital was then determined by writing and solving simultaneous equations using the observed coupling constants for two protons. The coupling constants for the remaining protons were then calculated and compared with observed coupling constants. The results show that sigma delocalization is most important for these complexes, but that there is an important pi contribution. The unpaired spin placed in the pi orbital arises from a spin polarization mechanism centered on the nickel(II) ion.

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RELAXATION METHODS IN KINETIC STUDIES

Kathy Myers

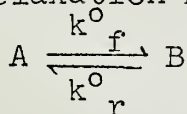
February 18, 1969

Introduction

Since about 1955, relaxation methods have been increasingly used to obtain kinetic data on fast reactions in equilibrium systems. If a chemical equilibrium is subjected to perturbation by a rapid change of external parameters such as temperature, pressure, or electrical field density, the equilibration to the new conditions will proceed with a time lag that is uniquely related to the rate constants of the system. In a multiple-step system, the process is characterized by a whole spectrum of relaxation times, which can be expressed in terms of the rate constants by well-defined mathematical transformations.¹ Rate constants covering the range from 5 sec^{-1} to $10^9 \text{ M}^{-1} \text{ sec}^{-1}$ are currently available.

Theory

The basic theory of relaxation methods can be described using the simple equilibrium system



plied, making it $A \xrightleftharpoons[k_r]{k_f} B$.

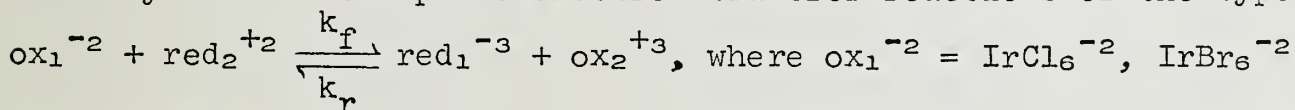
Define A_0, B_0 - initial concentrations of A and B
 \bar{A}, \bar{B} - new equilibrium concentrations of A and B
 A, B - instantaneous concentrations of A and B
 $X = A - \bar{A} = \bar{B} - B$ (distance from equilibrium)

Then
$$\begin{aligned} \frac{-dA}{dt} &= \frac{-dx}{dt} = k_f A - k_r B \\ &= k_f (\bar{A} + x) - k_r (\bar{B} - x) \\ &= (k_f + k_r) x \end{aligned}$$

and $\tau = (k_f + k_r)^{-1}$ is the relaxation time for the system. Thus, if τ and K_{eq} are determined experimentally, k_f and k_r may be evaluated.²

Applications

Discussion of some specific but typical uses of relaxation methods may be helpful. Hurwitz and Kustin¹⁰ used the temperature jump method to study fast outer-sphere electron-transfer reactions of the type

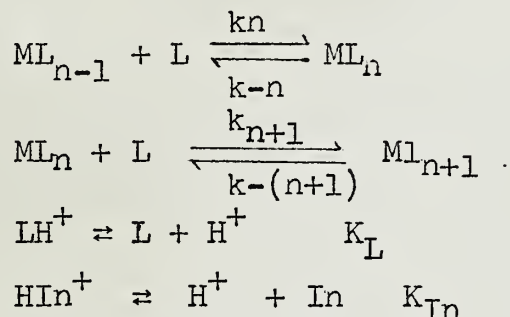


and $red_2^{+2} = 5,6\text{-dimethyl-1,10-phenanthroline iron(II)} = Fe(DMP)_3^{+2}$
 $= 4,7\text{-dimethyl-1,10-phenanthroline iron(II)} = Fe(4,7\text{-DMP})_3^{+2}$
 $= 4,4'\text{-dimethyl-2,2'-bipyridine iron(II)} = Fe(DMBPY)_3^{+2}.$

Temperature-jump methods make use of the relation $\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$, and utilize the discharge of a capacitor through the sample to cause temperature jumps on the order of 10°C in 10^{-6} seconds.

Hurwitz and Kustin showed that the relaxation time for the system, with equal initial concentrations of reactants A_0 and no products, was related to the rate constants by $1/\tau = 2k_1 A_0 \sqrt{K}$. Their experimental results indicated that most of the rate constants for these reactions were diffusion-controlled or close to it, that free energy considerations were more important than coulombic attractions in determining the rate of reaction, and that steric restrictions might be one reason that the rate constants fell short of the theoretical diffusion limit.

A more complicated system was examined by Hammes and Steinfield,¹¹ again using temperature jump techniques. They studied Ni(II) and Co(II) complexes with one, two, or three glycine, diglycine, or imidazole molecules, using a pH-indicator to follow the relaxation of systems like



They assumed that the last two reactions were much faster than the first two, and hence at equilibrium at all times. The relaxation times for the system were then shown to be $1/\tau_{1,2} = \frac{(a_{11}+a_{22}) \pm 1/2\{(a_{11}+a_{22})^2 - 4(a_{11}a_{22}-a_{21}a_{12})\}^{1/2}}{2}$

$$\begin{aligned} \text{where } a_{11} &= k_n \left(\frac{\overline{\text{ML}}_{n-1}}{1+\alpha} + \overline{\text{L}} \right) + k-n & a_{22} &= k_{-(n+1)} + k_{n+1} \left(\frac{\overline{\text{ML}}_n}{1+\alpha} + \overline{\text{L}} \right) \\ a_{12} &= k-n - k_n \frac{\overline{\text{ML}}_{n-1}}{1+\alpha} & a_{21} &= k_{n+1} \left(\overline{\text{L}} - \frac{\overline{\text{ML}}_n}{1+\alpha} \right) \end{aligned}$$

$$\text{and } \alpha = \frac{[\text{H}^+]}{K_L + \overline{\text{L}} \left(\frac{K_{\text{In}} + [\text{H}^+]}{K_{\text{In}} + [\text{H}^+] + \overline{\text{In}}} \right)} \quad \text{is the correction term for the rapid}$$

protolytic equilibria and is, conveniently, negligible in most of their experiments. Using the experimentally determined relaxation times and known equilibrium constants for complex formation, they determined the various rate constants by a trial and error method. They then attempted to relate these to the rate of expulsion of the first water molecule from the inner hydration sphere of Ni(II) or Co(II), and found that this was approximately twenty-five times faster for Co(II). From the trend in rate constants as an additional ligand was added, they postulated

that diglycine was bonded through the peptide oxygen rather than the carboxyl group. They also concluded from the ratios of the rate constants of Ni(II) and Co(II) in identical bonding systems that the difference in activation energy between the two was about 2kcal/mole, compared to 4.9 kcal/mole predicted for hexa-aquo ions on a crystal-field model.¹²

Other relaxation methods which have been used are: 1) pressure jump, which is similar to temperature jump and depends on the relation $\frac{d nK}{dP} = \frac{-\Delta V}{RT}$, 2) electric impulse methods, which depend on the fact that increased field strength causes increased dissociation of weak electrolytes, and 3) sound waves, which cause fluctuations in temperature and pressure of the sample and give rise to an absorption of power when the sound frequency and reciprocal relaxation time are of the same order.^{1,2}

A wide variety of reactions has been studied, some using quite ingenious methods of producing relaxation situations and evaluating data. Metal-ligand complex formation has been extensively studied.¹³⁻¹⁶ Ion pairing,¹⁷ dissociation of substituted organic acids,¹⁸ proton transfer,¹⁹ and enzyme systems^{20,21} are only a few of the many types of systems that have been investigated. Transient intermediates in non-equilibrium systems have been studied by combining stopped flow and temperature methods.²² Relaxation methods are likely to continue to be a most useful and widely-applicable means of studying the kinetics of very fast reactions.

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AN INVESTIGATION OF THE CHRONOPOTENTIOMETRIC OXIDATION OF

Pt(II) - Sn(II) COMPLEXES

Denis F. De Craene

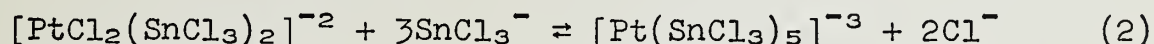
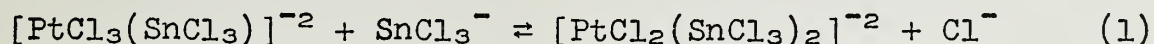
February 20, 1969

In recent years there has been a good deal of interest in bimetallic complexes of platinum(II) and tin(II) (1-5). The results of synthetic and structural investigations (6,7) have shown that the platinum and tin atoms participate in metal-metal bonding interactions. Parshall (8) has investigated the nature of this interaction through the use of F^{19} n.m.r. shielding parameters. The conclusion is that $SnCl_3^-$ is a poor σ -donor and a strong π -acceptor ligand. Yamamoto (9) employed potentiometric analysis to follow the reduction of platinum(IV) to platinum(0) by addition of tin(II). These workers observed the formation of a stable intermediate between platinum(II) and tin(II).

These observations led to the investigation presented in this seminar. Chronopotentiometry was selected as an electrochemical technique which, although simple in instrumental design, would supply information about the nature of the complexes in solution, the oxidation states of the platinum and tin atoms involved in complexation, and also, some insight into the effect of coordination of tin(II) on the electrode characteristics of platinum(II). An acidic chloride medium was chosen because it presented the least difficulty in an electrochemical approach to the problem.

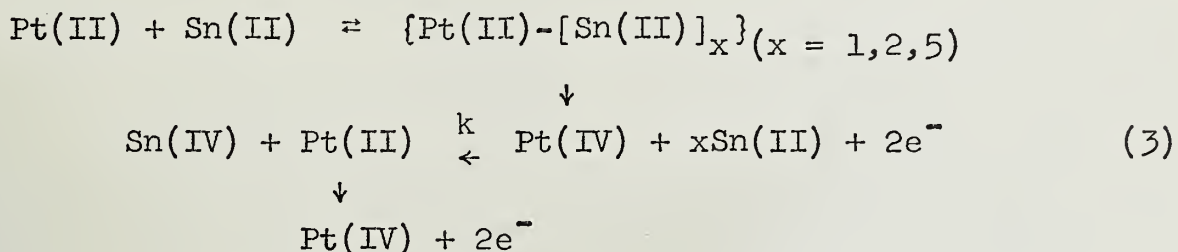
The chronopotentiometric oxidation of $PtCl_4^{2-}$, and of $SnCl_3^-$, were investigated for the purpose of comparison. Both species undergo oxidation from the +2 to the +4 states in one-step, irreversible processes which are diffusion controlled. The electrode processes occur at +0.725v and +0.575v (vs an Ag/AgCl reference electrode) for $PtCl_4^{2-}$ and $SnCl_3^-$ respectively.

Systems containing platinum(II) and tin(II) in stoichiometric ratios of 2:1, 1:1, 1:2, and 1:3 were found to contain bimetallic complexes of the composition $[Pt(Cl)_{4-x}(SnCl_3)_2]^{2-}$, where $x = 1, 2$ and is determined by the molar ratio of tin(II) to platinum(II). Evidence for the formation of $Pt(SnCl)$ was also obtained. The formation of 1:3 and 1:4 bimetallic complexes must be considered as intermediates having only transient existence in solution. In systems which were prepared with platinum(II) in excess or equivalent amounts to tin(II), only the 1:1 bimetallic species was found and complexation consumed all of the tin(II). In systems excess tin(II), the following equilibrium were encountered:



Values of $1.20 \times 10^3 \text{ M}^{-1}$ and $3.82 \times 10^6 \text{ M}^{-3}$ were calculated for the equilibrium constants in eq. (1) and eq. (2) respectively.

The electrode processes associated with the bimetallic complexes are irreversible and the mass transport processes are kinetically complicated. On the basis of quantitative interpretation of the kinetics, the following mechanism was proposed:



The rate constant, k , which describes the redox reaction following the electrode reaction was estimated to within an order to be $10^5 \text{ sec}^{-1} \text{ M}^{-1}$.

Quantitative treatment of the electrode reaction proper was not carried to the point of proposing a mechanism for the electron transfer step. Such a treatment is beyond the scope of this work. It was interesting to note that the tin(II), upon coordination to platinum(II) in a bimetallic complex, becomes the more noble of the two metals. The effect of this complexation upon platinum(II) was to make it more easily oxidized at the electrode as the number of tin atoms in the coordination sphere increased.

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NOBLE GAS CHEMISTRY

George F. McKnight

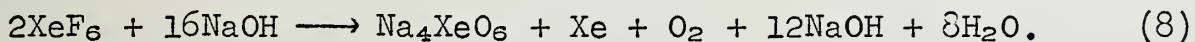
March 4, 1969

Introduction

In 1962 Neil Bartlett of the University of British Columbia accomplished what had eluded chemists for over a half a century: he succeeded in preparing a stable noble gas compound, xenon platinum hexafluoride, XePtF_6 (1). Bartlett's experiment destroyed the long-held hypothesis that the noble gases would not react to form stable compounds. The formation of XePtF_6 catalyzed a tremendous interest in this new field of chemistry. Within a year of Bartlett's discovery a symposium on noble gas compounds was held at Argonne National Laboratories which resulted in a book surveying the work accomplished in this new field (2). For those interested in a more detailed description of the early work on noble gas compounds, I strongly recommend this book.

Experimental

The success of Dr. Bartlett with xenon prompted Claassen, Selig, and Malm (3) of Argonne National Laboratories to attempt the direct thermal combination of xenon and fluorine in an effort to form xenon fluoride. They succeeded in preparing an equilibrium mixture of three fluorides: XeF_2 , XeF_4 , and XeF_6 . The di- and tetrafluorides have been prepared also by electric discharge (4) and by irradiation of gaseous mixtures of xenon and fluorine with ultraviolet light in the 2200-3400 Å region (5). The fluorides were identified by use of infrared and mass spectrophotometry (6). Reaction of XeF_6 with a limited amount of SiO_2 or H_2O yields the compound xenon oxytetrafluoride, XeOF_4 (7). Reaction of XeF_6 with excess SiO_2 or H_2O yields the highly explosive xenon trioxide, XeO_3 (7). Hydrolysis of XeF_6 in strongly alkaline solutions results in the precipitation of stable perxenate salts according to the equation:



Addition of sodium perxenate to concentrated sulfuric acid yields xenon tetroxide, XeO_4 (9). Spittler and Jaselskis (10) have reported that mixing equal volumes of aqueous XeO_3 and alkali hydroxide yields stable mono-alkali xenates, MHXeO_4 , where $\text{M} = \text{Na}^+$, K^+ , Cs^+ , Rb^+ .

The only other noble gases which have entered into stable compound formation are krypton and radon. A krypton fluoride has been prepared by the electric discharge method (12) and analyzed as KrF_2 . Grosse, *et. al.* (11) have reported the formation of KrF_4 , but thus far, the preparation has not been reproducible. Radon, because of its low ionization potential, would be expected to form the most stable compounds, but because of the high radioactivity of radon, such compounds are difficult to prepare and decompose rapidly. Fields, *et. al.* (13) have prepared a radon fluoride using the nickel vacuum line technique, but were unable to analyze their compound because of inability to remove it from the vacuum line.

The inertness of the remaining noble gases has been attributed to their high ionization potentials. It does not seem probable that enough energy can be gained in bonding to compensate for the large energy necessary to effect formation of such bonds.

Characterization

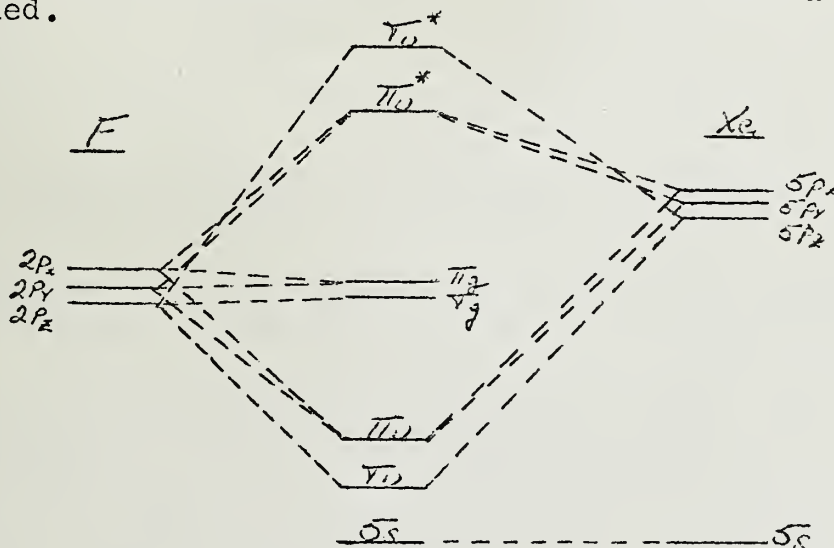
Unlike radon fluoride, most noble gas compounds have been characterized without unusual difficulty. The xenon fluorides are all colorless solids at room temperature. Infrared and Raman studies indicate that KrF_2 and XeF_2 are linear molecules in the vapor phase. Siegel and Gebert (14) performed an X-ray study on the solid XeF_2 and determined its unit cell as tetragonal with the xenon atoms occupying the corners and the body centers of the cells. The Xe-F distance determined from neutron diffraction (15) was 2.00 ± 0.01 Å. A study of the infrared spectrum of XeF_4 led to the assignment of a square planar structure for the molecule in the vapor phase. An X-ray study (14) showed solid XeF_4 to have a square planar molecular structure with a monoclinic unit cell. By neutron diffraction (16) the interbond angles were evaluated as $90.0 \pm 0.1^\circ$ and the Xe-F bond lengths found equal at 1.95 ± 0.01 Å. Claassen, Chernick, and Malm (17) noted the close correspondence between the vibrations of XeF_4 and those of XeOF_4 , a colorless liquid. This close correspondence led to the assignment of a square pyramidal structure to the XeOF_4 molecule. It is believed that the O-Xe-F angle is close to 90° . Martin and Wilson (18) studied the pure rotational spectrum of XeOF_4 in the microwave region and found 1.70 Å for the Xe-O bond length, 1.95 Å for the Xe-F distance, and $91 \pm 2^\circ$ for the O-Xe-F angle. The compound XeO_3 was shown to have an ammonia-like structure in the solid form by use of infrared spectroscopy (19). An X-ray study by Templeton, et. al. (20) confirmed this structure and reported Xe-O distances of 1.76 Å and an interbond angle of 103° . The oxide XeO_4 was determined to have a tetrahedral molecular structure from a vapor phase infrared study (21). An approximate Xe-O bond distance of 1.60 ± 0.2 Å was determined from the infrared spectrum.

Bonding

The bonding in noble gas compounds has been explained in terms of the valence bond theory and the molecular orbital theory. The valence bond or hybrid bond approach is useful in predicting the molecular geometry for the noble gas compounds. For the difluorides, there are five electron pairs (three lone pairs and two bonded pairs) which can be distributed in a trigonal bipyramid around the xenon atom with the lone pairs in the plane of the triangle giving a linear geometry. In the molecule, XeF_4 , there are six electron pairs distributed octahedrally around the xenon atom with the lone pairs trans to each other giving a square planar configuration. Extension of these to the XeF_6 molecule would give an unsymmetrical molecule with the one lone pair of electrons distorting the octahedral geometry. An unsymmetrical set of hybrids of this type is relatively rare, and Coulson (22) points to the existence of XeF_6 as evidence of the inadequacy of the hybrid bond model of these compounds. However, Bartell, et. al. (23) have made a preliminary electron diffraction study of XeF_6 in the gas phase and reported that

the symmetry of the molecule is less than octahedral, which lends some support to the valence bond prediction of a distorted octahedron. Despite its shortcomings, the valence bond approach allows one to explain the geometries of the noble gas compounds. However, in order to explain many of the other properties of the noble gas compounds, molecular orbital theory must be used.

The molecular orbital approach is based on the assumption that, in the xenon fluorides, bonding occurs primarily through overlap of the 2p orbitals of the fluorine atoms with the 5p orbitals on the xenon atom giving three center bonds. The p orbitals can overlap to give sigma and pi bonds. For the XeF_2 molecule, there result three molecular orbitals due to sigma overlap of the p_z orbital on the three centers and a set of three doubly degenerate molecular orbitals resulting from pi overlap of the p_x and p_y orbitals. The arrangement of these molecular orbitals in an energy level diagram is shown below. The xenon atom contributes eight electrons, whereas each fluorine atom contributes five electrons for a total of 18 electrons. Thus, only the σ_u^* orbital will remain unoccupied.



One criticism which has been leveled against this molecular orbital treatment of the noble gas compounds is its prediction of an undistorted octahedral symmetry for the XeF_6 molecule.

Summary

In recent years, the area of noble gas compound preparation has reached a plateau in that no new simple stable compounds have been formed. Whether the noble gases will react to give stable compounds other than oxides and fluorides is a question only time will answer. Chemists, having once been proven wrong, are very reluctant to give a simple yes or no answer to the question.

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STUDIES OF THE EFFECTS OF FLASH HEATING ON CATALYTIC SURFACES

W. Ronald Cares

March 18, 1969

The process of flash heating a solid material by means of a capacitor discharge lamp in order to vaporize the material and to create transient chemical species has been recently investigated (1-3). The effects of such high intensity light pulses illuminating the surface of a lightly colored, finely divided solid have not been adequately investigated. The temperature pulse resulting from such illumination of a catalyst might cause measurable changes in its catalytic properties.

We have attempted to study these effects in an effort to relate any observed changes in the catalytic properties of alumina to direct effects of the photoflash. The dehydration of ethanol on γ -alumina was chosen as the system to be used for this study.

The dehydration of ethanol to diethyl ether and to ethylene on alumina has been known since the late 1700's. Diethyl ether production begins on alumina at about 180°C while ethylene production does not occur below temperatures of about 240°C. Several recent reviews concerning the dehydration of ethanol and other alcohols on alumina are available (4-6).

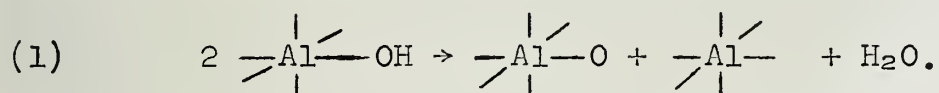
Although the major products of the dehydration reaction of ethanol on alumina have been well established, considerable doubt still exists concerning the mechanism of the reaction. In the 1920's, investigators observed that the yield of diethyl ether reached a maximum value with increasing reaction temperature whereas the ethylene yield continually increased with increasing reaction temperature (7-9). The reverse reactions of diethyl ether to ethylene and water or to ethylene and ethanol were also observed on alumina (8). The gross mechanistic picture resulting from these studies was that ethanol was dehydrated to diethyl ether and, at higher temperatures, the ether was readsorbed by the catalyst and dehydrated to ethylene. Later, the possible concurrent dehydration of ethanol directly to ethylene was included in this scheme.

Earlier investigators of the ethanol dehydration reaction were hampered by the unavailability of sensitive analytical techniques for accurate analysis of reaction products occurring upon the dehydration of less than 5% of the ethanol. Development of the gas chromatographic technique has since alleviated this problem.

The earliest investigators did not realize that different crystalline modifications of alumina exist and that the different aluminum hydroxides can be stable to between 300° and 400°C (10). Much early work was undoubtedly performed on alumina catalysts having a considerable aluminum hydroxide content.

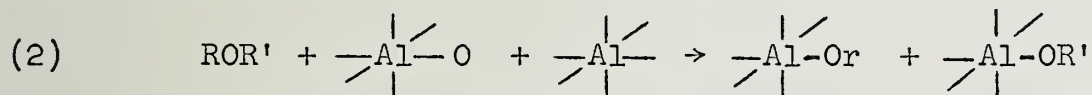
The gamma form (American nomenclature) of aluminum oxide is the form most used as a catalyst. Gamma alumina is stable at temperatures up to about 850°C (10) and has been characterized as having a distorted

spinel structure (11). Gamma alumina has a porous particle structure yielding surface areas of about 100 m²/g to 250 m²/g and at room temperature the surface is covered with hydroxyl groups and adsorbed molecular water. All molecular water is removed from the alumina surface on heating to slightly below 200°C whereas complete removal of the surface hydroxyl groups does not occur until temperatures of 1100° to 1200°C are reached (12). Heating of the alumina catalyst at increasing temperatures from about 200°C results in the increasing condensation of surface hydroxyl groups with the elimination of molecular water. The condensation of surface hydroxyl groups produces high energy sites containing an exposed oxygen atom held by an underlying octahedral aluminum atom and an adjacent exposed aluminum atom on the surface (13):



Such a high energy site has also been pictured as a strained Al-O-Al linkage (14). The tetrahedral sites are supposedly not involved in these reactions.

Infrared investigations of ethanol adsorbed on alumina indicate the presence of ethoxide groups on the surface at temperatures above 135°C and small numbers of a carboxylate-type group at temperatures above 160°C (15, 16); physical adsorption of molecular ethanol is observed only below 150°C (16). Diethyl ether has also been found to give ethoxide groups when adsorbed on alumina surfaces. Our work suggests that reaction (2) occurs.



All previous investigations of the reaction of ethanol on alumina have been conducted in flow reactors where ethanol vapor is continuously passed through a bed of alumina catalyst. Analysis of reaction products has usually been conducted on the gases leaving the catalyst bed after the system has reached a steady state. In such a system the catalyst surface becomes saturated with not only the reactant ethanol but also the products of the reaction. Secondary reactions involving products are made possible in such a system.

The reactor used in our study is of the microcatalytic type as developed by Hall and Emmett (17) and has been used extensively by Hall, et al. This microcatalytic reactor system consists of a four inch length of 1/8 in O.D. aluminum tubing containing approximately 10 mg of the alumina catalyst. The reactor assembly is inserted between the sample injection port and analytical column of a Perkin-Elmer model 820 gas chromatograph. A separately controlled oven is provided for the reactor. Ethanol, or other reactant, is injected into the chromatograph in pulses or slugs through the normal injection port and allowed to react on the alumina; the reaction products and unreacted ethanol are then swept from the catalyst by the flowing carrier gas directly into the analytical column for analysis.

The helium carrier gas is purified and rendered absolutely free of water by passing it through a liquid nitrogen cooled pre-column of 13x molecular sieve powder. A Porapak Q analytical column has been found to be best suited for the separation of ethylene, water, ethanol

and diethyl ether. The liquid volume of reactants injected into the chromatograph ranged from 0.10 to 1.00 microliter, 0.30 microliter corresponding to 5.1 micromoles of ethanol at room temperature.

The microcatalytic reactor system as described is a differential reactor and as such should yield initial reaction rates when pure reactant is injected. The reaction of ethanol on alumina is found to be a zero order reaction throughout the temperature range of about 190° to 360°C. For initial rates of a zero order reaction, the apparent Arrhenius type activation energy is found from the slope of the line resulting from plotting the logarithm of the product yield versus the reciprocal absolute temperature of the reaction. The assumption is made that, under our reaction conditions, the product yield is proportional to the reaction rate at each temperature. Such a treatment demands that the reaction duration be the same at all reaction temperatures. A similar treatment has recently been used for a flow-type reactor study (18).

Two types of commercial alumina were used in this study; both were supplied by the Harshaw Chemical Company. Al-0102P alumina was a lower activity alumina containing about 0.2% by weight sodium impurity and 0.01% by weight silicon impurity and having a surface area of $124 \pm 1 \text{ m}^2/\text{g}$ as determined in our laboratory. A sample of flash heated Al-0102P alumina was found to have the same sodium content but had 0.1% by weight additional silicon impurity. A higher activity Al-1401P alumina had 0.02% by weight sodium and 0.01% by weight silicon impurities; its surface area was about $180 \text{ m}^2/\text{g}$.

The Arrhenius plot for diethyl ether production from ethanol on Al-0102P type alumina produced both a high temperature and low temperature apparent activation energy. Only a high temperature apparent activation energy was observed for ethylene production. For the Al-1401P alumina only one apparent activation energy was observed for diethyl ether production while ethylene production showed different high and low temperature values. Table 1 shows the activation energies for ethylene and diethyl ether production on the various aluminas studied.

Table 1

APPARENT ACTIVATION ENERGIES FOR
ETHYLENE AND DIETHYL ETHER PRODUCTION FROM ETHANOL

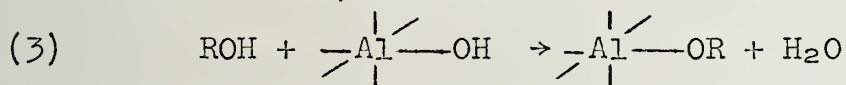
AVERAGE ACTIVATION ENERGY
kcal/mole, \pm Std. Deviation
(No. of Values Averaged)

<u>ALUMINA</u>	<u>ETHYLENE</u>		<u>DIETHYL ETHER</u>	
	<u>High Temp.</u>	<u>Low Temp.</u>	<u>High Temp.</u>	<u>Low Temp.</u>
Al-0102P	36.0 \pm 1.8 (6)		7.7 \pm 1.6(6)	48.8 \pm 7.8(6)
Al-0102P, Flash Heated	35.6 \pm 2.5 (5)		9.8 \pm 1.6(5)	37.4 \pm 3.0(5)
Al-1401P	30.9 \pm 1.0 (4)	44.5 \pm 3.9(3)	11.8 \pm 1.4 (4)	

The activation energies reported in the literature for the zero order reaction of ethanol to ethylene are 30.8 kcal/mole (19) and 33 kcal/mole (20). There is less agreement among those values reported for reaction to diethyl ether which are about 17 kcal/mole (19), about 27 kcal/mole (20) and 14.2 ± 0.2 kcal/mole (21). Our determinations of the apparent activation energy for ethylene production from diethyl ether as the reactant over Al-1012P alumina have values of 26.0 and 26.1 kcal/mole versus the reported literature values of 24.0 kcal/mole (22) and 28.5 kcal/mole (23).

Throughout the course of this study, the injection of an alcohol sample over an alumina catalyst produced eluted quantities of water in great excess over those quantities predicted on the basis of observed ethylene and diethyl ether yields. Simultaneously, large quantities of alcohol were lost on the basis of what was expected in the eluant by material balance. Excess water was not eluted when diethyl ether was reacted, but eluted ether was less than expected.

These material balance observations can be accounted for by assuming the formation of ethoxide groups on the alumina surface through reaction of either ethanol or diethyl ether with high energy surface sites (Reaction 2) or of ethanol with the surface hydroxyl groups:



Subsequent injection of water following either ethanol or diethyl ether injections reverses the surface reaction (Reactions 1 and 3), liberating large quantities of ethanol. Minute amounts of diethyl ether are also eluted when H₂O is injected, suggesting the possibility of additional reactions other than those indicated.

Injection of mixtures of dimethyl and diethyl ethers produces ethyl methyl ether as a major product. Injection of ethyl methyl ether produces both dimethyl and diethyl ethers. Subsequent water injections show only methanol and ethanol as the products desorbed following the ether injections. Injection of ethyl n-propyl ether yields both diethyl and di-n-propyl ethers as products while water desorption gives ethanol and n-propanol.

It was observed that during the dehydration of ethanol in the micro-catalytic reactor both the diethyl ether yield (observed initially at 190°C) and ethylene yield (observed initially at 240°C) increased as the reaction temperature was increased to 400°C. At no time in our experiments was a maximum in the diethyl ether yield observed.

It is now suggested that the formation of diethyl ether, and ethers in general, occurs on alumina by the reaction of two adjacent ethoxide groups on the surface. The formation of ethylene at higher reaction temperatures occurs by the reaction of a surface ethoxide group with an adjacent exposed oxygen atom.

Other reaction products which have not been previously reported for ethanol on alumina were found in our experiments to include methane, carbondioxide, 2-butanol or ethyl acetate, and 1-butanol. The dehydrogenation product of ethanol, acetaldehyde, was also observed at higher reaction temperatures.

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ION CYCLOTRON MULTIPLE RESONANCE AND ITS APPLICATION TO THE STUDY OF GAS-PHASE ION-MOLECULE REACTIONS

Eric F. Johnson

April 8, 1969

Introduction

In recent years, a new method of mass spectrometry has been developed which relates the motion of a charged particle in electric and magnetic fields to the particle's charge to mass ratio. Unlike other methods of mass spectrometry, the charge to mass ratio is detected through resonant absorption of power from a radio frequency field. In addition, ion-molecule reactions in the resonance cell may be studied by techniques analogous to those used in double resonance experiments in n.m.r. This seminar will describe the basic principles of this method and the nature of its applications.

Basic Theory

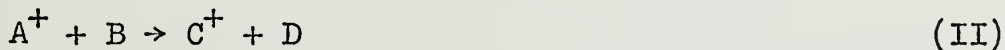
The motion of a particle of charge q and mass m in a uniform magnetic field of strength B is circular in the plane perpendicular to the magnetic field and unconstrained parallel to the field. The frequency of the motion, given by equation (I), is independent of the particle's velocity and dependent on the magnetic field strength

$$\omega_c = \frac{q}{m} B \quad (I)$$

and the charge to mass ratio of the particle. Knowledge of the cyclotron frequency and the magnetic field strength will allow the charge to mass ratio of the particle to be determined from equation (I).

When an alternating electric field of the same frequency as the cyclotron frequency of the ion is applied perpendicular to the magnetic field, the charged particle will be accelerated in a spiral motion of increasing radius. This results in an increase in power consumption by the sample. A plot of power absorption versus frequency will display the mass spectrum of the sample.

A reaction of the type shown in expression (II) will introduce a dependence of the product ion on the reactant ion.



Since the rate of the reaction and thus the number density of the product ion is expected to depend on reactant velocities, irradiation of the sample with a second alternating electric field at the cyclotron frequency of the reactant ion should result in a change in the spectrum of the product ion. Such experiments have been performed, and they may be used to study ion-molecule reactions (1).

Instrumentation

The spectrometer may be described as a hybrid of a conventional mass spectrometer's sample handling apparatus and the magnet and detection devices of an n.m.r. spectrometer. In those applications

we will consider, a marginal oscillator detection system with modulation and phase sensitive detection is widely used. For singly charged ions, a mass range of 1-200 a.m.u. is accessible with magnetic field strengths of 0-15,000 gauss and r.f. frequencies of 50 KHz. to 23 MHz. This is a convenient range for the use of previously developed n.m.r. marginal oscillator detection systems.

The modulation may be produced by modulating the ion current from the source region for which absorption spectra are obtained or by modulating the magnetic field or the marginal oscillator for which derivative spectra are obtained. In double resonance experiments, the second irradiating oscillator may be pulsed. The modulation of the product ion density will be induced by the ion-molecule reaction, provided it is sufficiently fast. Therefore, the pulsed double resonance spectrum will display directly the difference between the single and double resonance spectra for the product ion.

Although the spectrometer has a high resolution ($1/30,000$) and a high sensitivity (1 to 10 ions), its principle advantage lies in application of the double resonance method to the study of ion-molecule reactions. In addition, the residence time of the ion in the spectrometer is longer than that of an ion in a conventional mass spectrometer. Observable ions must be correspondingly longer-lived, and less stable species are less likely to be observed in i.c.r. spectrometers than in conventional instruments (1).

Applications

The double resonance technique has been applied to determination of ion-molecule reaction schemes in chloroethylene, mixtures of nitrogen and deuteromethane, charge-transfer in rare gas isotopes, alkyl halides(1), methanol(2), acetonitrile(3), diborane(4), p-dichloroethylbenzene(5), ethylene(6), and perfluoroethane(7).

In addition to determining those ions connected by a reaction sequence, the double resonance technique can yield information about the mechanism of a reaction. When compared to theoretically predicted isotope distributions, the double resonance spectra can determine whether an isotope in the product ion had its origin in the ionic reactant, in the neutral reactant, or in either. The reaction mechanism must be consistent with these results.

Some authors have attempted to relate the sign of the double resonance peak to the endo- or exothermicity of the ion-molecule reaction. Negative peaks are associated with exothermic reactions, and positive peaks with endothermic reactions. Although the sign of the peak can be related to the sign of (dk/dT) , where k is the rate constant and T is the reactant ion kinetic energy, the generalization above rests on experimental evidence. Indeed, it is rather difficult to find a simple relation between the quantity (dk/dT) and the enthalpy of reaction. Beauchamp and Batrill have used this observation to determine proton affinities for H_2O and H_2S by studying the ion-molecule reactions of H_3O^+ and H_3S^+ with a variety of neutrals for which there is thermodynamic data. His results are close to those determined by other methods.

Conclusion

Ion cyclotron resonance spectroscopy is a relatively new method which can yield information about ion-molecule reaction schemes and mechanisms. It may even be extended to quantitative studies, as the underlying theory is extended and a larger amount of experimental data is accumulated.

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APPLICATIONS OF THE WOODWARD-HOFFMANN RULES
TO TRANSITION METAL CATALYSIS

Joseph J. Brooks

April 22, 1969

Introduction

Complete stereospecificity is characteristic of a large class of known ring opening and cyclization reactions. In 1965, Robert Woodward of Harvard and Roald Hoffmann of Cornell published a series of communications¹⁻⁵ which extended simple molecular orbital theory to this area of reaction chemistry. Their approach correlates with respect to symmetry the molecular orbitals of reactants with those of the products. Using this approach, they have been able in recent years to rationalize and predict the stereochemical course of a great number of concerted organic reactions.

Of particular interest to the inorganic chemist are those reactions involving transition metals which seem to violate the Woodward-Hoffmann rules. The purpose of today's seminar will be to examine the role of the transition metal in some of these systems. The discussion will be limited to two types of reactions which Woodward and Hoffmann investigated: electrocyclic reactions and cycloaddition reactions.

Electrocyclic Reactions

An electrocyclic transformation is defined as the formation of a single bond between the termini of a linear system containing k π -electrons and the converse process. Rotations leading to the formation or breaking of this single bond are classified as conrotatory or disrotatory. If the considered rotation occurs in the same direction about both bonds involved, it is called conrotatory, while concerted rotation in opposite directions is called disrotatory.

Consider the two possible modes for the conversion of cyclobutene to butadiene. The molecular orbitals which one must consider are the four π -orbitals of butadiene ($\chi_1, \chi_2, \chi_3, \chi_4$), the π and π^* orbitals of the cyclobutene double bond, and the σ and σ^* orbitals of the single bond to be broken.

Examination of the symmetry of the conrotatory rotation on cyclobutene reveals that a twofold axis is continuously maintained throughout the transformation. Thus, the orbitals involved can be classified as symmetrical, (S), or antisymmetrical, (A), according to their symmetry with respect to this twofold. One of the basic rules upon which this method is founded is that for continuous electronic reorganization to occur, the symmetry classification of a particular orbital cannot change during the course of the reaction. Therefore, one can correlate the π , π^* , σ , and σ^* orbitals of cyclobutene to particular orbitals of butadiene. When such a correlation is made σ becomes χ_2 , π becomes χ_1 , π^* becomes χ_4 , and σ^* becomes χ_3 . Considering these correlations, one sees that the ground state configuration of cyclobutene ($\sigma^2\pi^2$) leads to the ground state configuration of butadiene ($\chi_1^2\chi_2^2$). Thus Woodward and Hoffmann concluded that this process should proceed thermally since it involves a ground state to ground state conversion.

Examination of the symmetry of the disrotatory rotation reveals that a mirror plane is maintained throughout the transformation. The orbitals involved can be classified according to their symmetry with respect to this mirror plane. Correlations between reactant orbitals and product orbitals can be made as in the case of the conrotatory mode. This correlates σ to χ_1 , π to χ_3 , π^* to χ_2 , and σ^* to χ_4 .

Using these correlations, the ground state of cyclobutene ($\sigma^2\pi^2$) would lead to an excited state of butadiene ($\chi_1^2\chi_3^2$) if the mode of transformation is disrotatory. However, if one were to excite the cyclobutene photochemically to give the first excited state configuration ($\sigma^2\pi\pi^*$), this would lead to the first excited state of butadiene ($\chi_1^2\chi_2\chi_3$). Thus Woodward and Hoffmann concluded that photochemically this conversion should proceed by a disrotatory mode.

Using similar treatments for other electrocyclic reactions, Woodward and Hoffmann derived the following rules: if a polyene contains $4n$ π -electrons (where $n=0$ or any integer), thermal reactions occur by conrotatory modes, and photochemical reactions by disrotatory modes; if the polyene contains $4n+2$ π -electrons, the modes are reversed.

Merk and Pettit have recently examined several systems involving cyclobutene--butadiene transformations.⁶ In the systems they examined, the conrotatory process (predicted by the Woodward-Hoffmann rules) cannot occur because of the constraints imposed by the nature of the rings to be formed. These systems have been catalyzed by metal ions (Cu^+ and Ag^+) to proceed by the "forbidden" disrotatory mode. Pettit has proposed that the disrotatory mode becomes allowed via an intermediate metal-olefin complex. Metal orbitals of appropriate symmetry interact with the cyclobutene orbitals to give an allowed pathway for the disrotatory conversion to butadiene.

Cycloaddition Reactions

A cycloaddition reaction involves the joining of two molecules to form a ring structure. An example of this would be the addition of two ethylene molecules to form cyclobutane. The assumed geometry of approach places the two ethylenes in parallel planes, one above the other, with their π -clouds lying above and below the planes. The symmetry of the orbitals involved can be classified with respect to two symmetry elements: σ_1 , a mirror plane passing through the centers of the two ethylene molecules, and σ_2 , a mirror plane parallel to the planes of the two ethylene molecules and midway between them. One can then classify the 4 π -orbitals of the reactant and the corresponding 4 σ -orbitals of the product as (S) or (A) with respect to the two mirror planes. Thus the orbitals are given double symbols SS, SA, AS, or AA, where the first symbol refers to symmetry with respect to σ_1 , and the second symbol to symmetry with respect to σ_2 . One can make correlations based on symmetry relating reactant orbitals to product orbitals. Making such a correlation, Woodward and Hoffmann predicted that the conversion of two ethylenes to cyclobutane should proceed photochemically but not thermally.

Norbornadiene (I) undergoes smooth dimerization to cyclobutane derivatives in the presence of zerovalent Fe,⁷ Ni,⁸ and Co⁹ catalysts, and quadricyclene (II) is reported to undergo isomerization to



norbornadiene (I) when catalyzed by various metals.¹⁰ These systems can be thought of as cycloadditions since they involve cyclization analogous to that of two ethylene molecules forming cyclobutane. The interesting thing about these reactions is that in the metal free system they are strictly forbidden by the Woodward-Hoffmann rules.

Mango and Schachtschneider have recently proposed a mechanism in which the metal orbitals combine with the olefin orbitals giving a set of occupied molecular orbitals of the symmetry required for an allowed path.¹¹ In this mechanism, the metal orbitals interact with the olefin orbitals in such a way that they rearrange the electron density in the olefin orbitals and make the thermal cycloaddition an allowed process.

Conclusion

There are several other reactions which suggest metal participation of this sort. This would suggest that there are many other reactions to which similar symmetry arguments could be applied. The role of symmetry in formulating these selection rules is one of convenience rather than of necessity. This stems from the desire to have a qualitative method of predicting the energy profile of a system as it undergoes a smooth transition from the initial to the final state. The lack of numbers in this type of treatment is what Woodward and Hoffmann feel is its greatest strength. They reason that precise numerical values have to result from some specific sequence of approximations. In working from symmetry considerations one is more aware of the limitations than he would be from deceptively authoritative numerical results.

Symmetry arguments of this type are not limited to organic or organometallic systems. Eaton¹² has recently extended a very similar treatment to formulate selection rules which deal with such things as tetrahedral--square planar isomerization, racemization in optically active tetrahedral complexes, and cis-trans isomerism of square planar complexes. With proper use and adequate knowledge of the limitations, symmetry considerations similar to those of the Woodward-Hoffmann treatment can be powerful tools in predicting the courses and consequences of many reactions.

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NMR STUDY OF PENTAFLUOROPHENYL DERIVATIVES AND ITS APPLICATION TO THE STUDY OF CHEMICAL BONDING IN INORGANIC COMPOUNDS

Lim Yau-Yan

April 29, 1969

Introduction

Nmr spectroscopy is a useful method of furthering the understanding of electronic interaction between a benzene ring and its substituents. Attempts have been made to relate the chemical shifts of meta- and para-carbon nuclei¹ and of other nuclei (protons² and borons³) attached to the ring at these positions to the π -electron charge densities. This seminar will deal with the Nmr studies made on pentafluorophenyl systems and the application of the results to the elucidation of the nature of chemical bonding in some selected inorganic compounds.

General Survey

F^{19} ($I = 1/2$) is the only naturally occurring isotope of this element. The ranges of observed coupling constants and chemical shifts in F^{19} resonance studies are large compared with those found in H^1 spectra. Compounds containing several differently shielded fluorine nuclei coupled by indirect spin-spin interaction often show simple 1st order type spectra and the spectra for pentafluorophenyl derivatives have been analyzed as AAKXX systems.⁴ Nmr spectra of the aromatic compounds of the type C_6H_5X ($X = \text{halogen, methyl, methoxy, } -Mo(CO)_5, -Pb(C_6H_5)_3, \text{ etc.}$) were first reported following the synthesis of these compounds in 1963.⁵ Two years later, I. J. Lawrenson⁶ reported the chemical shifts and spin coupling constants of similar compounds with $X = F, H, CH_3, CF_3, Cl, Br, I, OCH_3, CN, \text{ and } NH_2$. The chemical shifts for meta- and para-fluorine were found to be linearly related to the Hammett-Taft reactivity parameters σ_I and σ_R .⁷

$$\delta_P = -39.7\sigma_R^0 - 12.9\sigma_I + 154.4 \quad \text{mean deviation} = \pm 1.0 \text{ p.p.m.}$$

$$\delta_M = -7.2\sigma_R^0 - 5.3\sigma_I + 162.9 \quad \text{mean deviation} = \pm 0.5 \text{ p.p.m.}$$

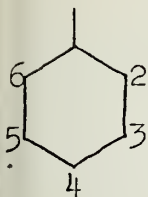
The chemical shifts of O-fluorine were not related to σ_R^0 and σ_I because of the so-called "ortho effect" which arises predominantly from an intramolecularly van der Waals effects.⁸

In 1966-69,⁹⁻¹² in a series of papers, W. A. G. Graham and his co-workers extended these studies to other systems and have examined over seventy pentafluorophenyl derivatives. Chemical shifts were correlated with coupling constants and their results were interpreted and explained in terms of Hammett-Taft reactivity parameters. Their findings will be discussed in the remaining part of the seminar.

Results

A close examination of their results reveal that the ortho coupling constants J_{23} and J_{34} varied little with substituents. No trends were detected for the para coupling constant J_{25} . Of the three meta coupling

X (1)



constants, J_{24} , J_{26} and J_{35} ; the first two showed correlations with the nature of the substituents. J_{24} was found to be linearly related to ϕ_P by the equation

$$J_{24} = -0.453\phi_P + 71.98$$

$$\text{RMS} = \pm 0.69 \text{ c.p.s.}$$

J_{24} and ϕ_M showed weaker correlation and the linear relation found was $J_{24} = -1.47 \phi_M + 239.3$ with RMS value of ± 1.7 c.p.s. Although J_{26} can be linearly related to ϕ_P , the RMS value (± 3.4 c.p.s.) indicates that the correlation is not good enough to be of predictive value.

The positions of the common organic substituents in the $J_{24}-\phi_P$ plot reveal an empirical relationship involving the electron-donor or acceptor properties of the substituents. Electron donating substituents such as $-\text{NH}_2$ and $-\text{OH}$ groups have high ϕ_P values with large negative J_{24} values. Electronegative substituents such as $-\text{CN}$, $-\text{COCl}$, etc., have low ϕ_P values with high J_{24} values. It was also found that the equations relating ϕ_P and ϕ_M to σ_R^0 and σ_I do not have identical coefficient in the σ_I term and the constant terms are also not equal. This finding is particularly significant because it invalidates the use of $(\phi_P - \phi_M)$ as a means of estimating resonance interactions as was done by F. G. A. Stone and his co-workers¹³ in the Nmr study of $\text{C}_6\text{F}_5\text{X}$ compounds. It should also be noted that in the equations obtained $\phi_P = -49.05\sigma_R^0 - 16.00\sigma_I + 153.72$

$$J_{24} = 21.00\sigma_R^0 + 6.21\sigma_I + 1.88$$

the coefficients of the resonance parameter are very much larger than those of the inductive parameter and it is therefore expected that ϕ_P and J_{24} can separately be related to σ_R^0 alone, giving reasonable straight lines as represented by the equations

$$\phi_P = -52.28\sigma_R^0 + 148.74$$

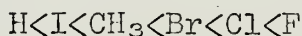
$$J_{24} = 22.26\sigma_R^0 + 3.81$$

This is the algebraic way of saying that both ϕ_P and J_{24} are sensitive mainly to resonance interactions.

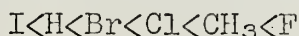
Applications

(1) Halogens

The ordering of halogens in the $J_{24}-\phi_P$ plot is of great interest. Although the ordering of the four halogens among themselves according to π -donor strength is the same in both phenyl and pentafluorophenyl systems, their positions relative to substituents with negligible π effects (e.g. $-\text{CH}_3$ and $-\text{H}$) are not. In the phenyl and monofluorophenyl series, the halogens are essentially weak π -donors with the order



However, halogens as substituents on the pentafluorophenyl ring appear to be much weaker π -donors and the order of π -donor strength is



so that with the exception of fluorine they might be considered as π -acceptors. The apparent disagreement in the ordering can be explained by the different polarity of the ring-halogen σ -bond in the two systems. Polarity of the bonds can be used to reconcile the two apparently opposite conclusions as to halogen-metal π -interaction in the series of square planar platinum(II) complexes of the type $\text{trans}[\text{Pt}(\text{X})\text{C}_6\text{F}_5(\text{PEt}_3)_2]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{CH}_3$) and the corresponding monofluorophenyl platinum complexes.

(2) Phosphines

The $J_{24}-\emptyset_p$ plot indicates that they range from weak π -acceptors to strong π -acceptors. The intermediate π -acceptor property of the metal carbonyl derivatives can be rationalized by the competition between the filled metal d orbitals and the benzene ring π electrons for access to the vacant d orbitals of phosphorous. The ($p \rightarrow d$) π bond in this compound is therefore not as strong as in the $-\text{BCl}_3$ complex. Among the series $\text{C}_6\text{F}_5(\text{C}_6\text{H}_5)_2\text{X}$, the π -acceptor character increases along the series free phosphine $< \text{Mo}(\text{CO})_5 \sim \text{Cr}(\text{CO})_5 \sim \text{Fe}(\text{CO})_4 \sim \text{W}(\text{CO})_4 < \text{S} < \text{O} < \text{BCl}_3 < \text{H}^+\text{Cl}^-$. The lone pair is effectively removed when the phosphorous expands its coordination to five. Thus π withdrawal from C_6F_5 increases along the series $(\text{C}_6\text{F}_5)_3\text{P} < (\text{C}_6\text{F}_5)_3\text{PF}_2 < (\text{C}_6\text{F}_5)_3\text{PS} < (\text{C}_6\text{F}_5)_3\text{PO}$.

(3) Group IV derivatives of oxygen and sulfur

Compounds studied belong to the series $\text{C}_6\text{F}_5-\text{X}-\text{MR}_3$ where X is oxygen or sulfur, M is Si, Ge, Sn or Pb and R is a methyl or phenyl groups. Sulfur compounds are well separated from the analogous oxygen compounds in the $J_{24}-\emptyset_p$ plot. This is attributed to back-donation of ring π -electrons to the vacant d orbitals of sulfur which reduces the net π -donor strength to almost zero.

The positions of the compounds in the plot indicate that the tendency to form π bonds with oxygen (or sulfur) decreases in the series $\text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$. It also indicates that silicon and germanium are π -acceptors, while tin and lead are π -donors relative to hydrogen. These estimates of the π -acceptor properties of the Group IV metals are in general agreement with conclusion drawn from base strength measurements.¹⁴⁻¹

(4) The pentafluoroaniline derivatives

In the series, $\text{C}_6\text{F}_5-\text{N}(\text{H})\text{R}$, π donation by R to the pentafluorophenyl ring was found to increase in the order $\text{B}(\text{C}_6\text{H}_5)_2 < \text{CH}_3 \sim \text{Si}(\text{CH}_3)_3 \sim \text{H} < \text{Sn}(\text{CH}_3)_3$. An interesting conclusion that can be drawn from the $J_{24}-\emptyset_p$ plot is that there is no appreciable π character in the nitrogen-silicon bond in N-trimethylsilylpentafluoroaniline. This is in sharp contrast to the used-to-be-accepted notion that there is considerable $p \rightarrow d$ π bonding in N-Si bond as a consequence of the planar structure of trisilylamine.

(5) Tin compounds

The range of values of \emptyset_p and J_{24} is not large and perhaps not justified to make an extensive discussion of the nature of bonding. However, the \emptyset_p values for the compounds $\text{C}_6\text{F}_5-\text{Sn}(\text{C}_6\text{H}_5)_3$ and $\text{C}_6\text{F}_5-\text{Sn}(\text{C}_6\text{H}_5)_2\text{Mn}(\text{CO})_5$ are consistent with the finding that the tin-manganese

bond is multiple in character,^{17,18} involving donation of electron density from filled 3d manganese orbitals to vacant 5d orbitals of tin.

(6) The pentafluorobenzonitrile complexes

The ρ_p and J_{24} values are consistent with the fact that complexing of pentafluorobenzonitrile with BF_3 and BCl_3 should increase the π -withdrawing ability of the $-\text{CN}$ group in the order $\text{BCl}_3 > \text{BF}_3$. However, complexing pentafluorobenzonitrile with BBr_3 , the strongest of the three acids gives the anomalous result of decreasing the π -acceptor property to below that of the $-\text{CN}$ group itself. Since the benzonitrile complexes were not isolated by the authors or fully characterized, the interpretation of these results still awaits further investigation.

Conclusion

The measurements of coupling constants J_{24} and p-fluorine chemical shifts in pentafluorophenyl derivatives can lead to some valuable information on the nature of π -interaction and one might use this method to study the nature of acid-base interaction.

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STRUCTURAL AND SPECTROSCOPIC STUDIES OF CERTAIN TRANSITION METAL HALIDES

Gary McPherson

May 6, 1969

Introduction

Double salts of the type RMX_3 (where R is a large monovalent cation, M a divalent first row transition metal ion, and X chloride or bromide ions) have been known for some time.¹ The crystal structures of several of these compounds have been determined.^{2,3,4,5,6,7,8} With the exception of $CsCuCl_3$, all of the structures are quite similar and can be thought of as consisting of infinite parallel linear chains of octahedra sharing faces. The transition metal ions occupy the centers, the halide ions the corners, while the cations hold positions between chains. The metal-metal distances within a chain are relatively short, and previous work indicates that magnetic coupling between ions might be significant. Therefore, it seemed that these compounds would make interesting, yet simple systems, for careful structural and spectroscopic studies.

Electron Spin Resonance Spectra

In order to find a suitable host lattice for single crystal esr work, the compound cesium magnesium trichloride was prepared. This was shown by x-ray structural analysis to be isostructural with the other RMX_3 compounds. The bromide salt was also prepared and found to be isostructural. The coordination about the magnesium ion in these compounds is octahedral with a slight trigonal distortion. The esr spectra of V^{+2} , Mn^{+2} , and Ni^{+2} were studied in both lattices at room and liquid nitrogen temperatures. In general, the observed spectra are typical of those seen for these ions in other lattices having trigonal symmetry. In addition, however, splittings due to hyperfine interaction of the unpaired electrons with ligand nuclei are clearly seen in the spectra of V^{+2} and Mn^{+2} in the bromide salt. This is direct evidence of significant metal to ligand electron delocalization in these compounds.

Optical Spectra

The polarized crystal spectra of $CsNiCl_3$, $CsNiBr_3$, and of these salts diluted in the analogous magnesium compounds were studied at room and liquid nitrogen temperatures. The general features of the spectra are typical of octahedral nickel(II). The only striking difference between diluted and undiluted spectra is in the intensities of the spin forbidden (triplet to singlet) bands. These transitions are much more intense in the pure compounds than in the diluted systems. Thus, it appears coupling between metal ions is responsible for much of the intensities of these forbidden bands. This is in agreement with some recent work by McClure on the spectra of certain manganese(II) compounds.⁹

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STRUCTURAL STUDIES OF ORGANOMAGNESIUM COMPOUNDS

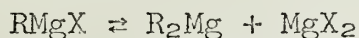
Joe D. Toney

May 13, 1969

Organomagnesium compounds may be classified into two groups: the Grignard reagents, RMgX , and the dialkyls and diaryls, R_2Mg . Because of their extensive use as synthetic intermediates, the nature of the structure of the Grignard reagents has been the source of much controversy for over sixty years and the question of whether the formula RMgX (R = organic group, X = halide atom) adequately represents these compounds has never been completely resolved.^{1,2} R_2Mg compounds have been prepared and studied only recently.³ These compounds present interesting structural problems with reference to the degree of association and solvation.

Alkylmagnesium Halides

The Grignard reagent is prepared by reacting an organic halide with magnesium in a Lewis base solvent. Schlenk⁴ observed that addition of dioxane to Grignard solutions yielded magnesium halide-dioxane complexes and proposed the equilibrium



to explain his results.

Slough and Ubbelohde⁵ measured the association values of several Grignard species in diethyl ether. They found that the degree of association varied widely with concentration. Vreugdenhil and Blomberg⁶ repeatedly recrystallized ethylmagnesium bromide from diethyl ether to remove excess MgBr_2 . They determined association values indicating the specie in solution is $\text{C}_2\text{H}_5\text{MgBr}(\text{C}_4\text{H}_{10}\text{O})_x$. In diethyl ether, Ashby⁷ found alkylmagnesium bromides and iodides to be essentially monomeric at low concentrations, becoming associated only at high concentrations. Chlorides, however, were found to be associated at all concentrations. A compound with the composition RMg_2X_3 has been isolated from an ethylmagnesium chloride-tetrahydrofuran solutions.⁸ A molecular weight study of ethylmagnesium bromide in triethylamine indicates a 1:1 RMgX :solvent ratio.⁹ The Grignard compound reportedly crystallizes from triethylamine as a disolvated monomer and loses one solvent molecule upon drying to give a 1:1 complex.

The infrared spectra of Grignard compounds in tetrahydrofuran and diethylether have been found to be very similar to their dialkyl analogues.¹⁰

Evans and Maher¹¹ found the chemical shifts of several Grignard species to be nearly identical to those of the analogous dialkyl compounds. Their data indicate that in most cases it is impossible to differentiate between the proton chemical shifts of dialkylmagnesium compounds and Grignard reagents. A plot of the proton chemical shifts of the coordinated ether groups versus concentration for several Grignard species show inflection points at 0.5 $\frac{\text{moles } \text{RMgX}}{\text{moles ether}}$ indicating

the possible formation of $\text{RMgX} \cdot 2\text{C}_4\text{H}_{10}\text{O}$.¹² The simultaneous existence of RMgX and R_2Mg species in diethylether solution has been demonstrated for pentafluorophenylmagnesium bromide and bis-(pentafluorophenyl)magnesium.¹³

The concern about the nature of the structures of alkylmagnesium halides has prompted X-ray investigations of several species. $\text{C}_6\text{H}_5\text{MgBr} \cdot 2\text{C}_4\text{H}_{10}\text{O}$ ¹⁴ and $\text{C}_2\text{H}_5\text{MgBr} \cdot 2\text{C}_4\text{H}_{10}\text{O}$ ¹⁵ were found to be four coordinate monomers. On the other hand, methylmagnesium bromide-tetrahydrofuran is a five coordinate monomer.¹⁶ The influence of the steric requirements of the solvent molecule on structure is also apparent in the comparison of $\text{MgBr}_2 \cdot 2\text{C}_4\text{H}_{10}\text{O}$,¹⁷ a four coordinate monomer, versus $\text{MgBr}_2 \cdot 4\text{C}_4\text{H}_8\text{O}$,¹⁸ a six coordinate monomer. The results of the X-ray studies provide evidence that the Grignard reagent can exist in the form of the unsymmetrical RMgX moiety. However, several association studies indicate the existence of dimeric and higher associated species in solution.

Crystallographic studies of ethylmagnesium bromide-triethylamine, ethylmagnesium chloride-tetrahydrofuran, and isopropylmagnesium chloride-diethylether were undertaken in order to determine the degree of association in these compounds. The crystal structure of ethylmagnesium bromide-triethylamine shows the compound to be a bromine bridged dimer with trans solvent groups. Ethylmagnesium chloride-tetrahydrofuran, $(\text{C}_2\text{H}_5\text{Mg}_2\text{Cl}_3 \cdot 3\text{C}_4\text{H}_8\text{O})_2$, is a dimer containing five four membered $(\text{MgCl})_2$ bridging units, five and six coordinated magnesium atoms, and a three coordinate chlorine atom. An analysis of these structures indicates that the degree of association depends upon steric effects and that the greater electronegativity of the chlorine atom versus the bromine and iodine atoms increases the probability of chlorine compounds forming bridging species.

R_2Mg Compounds

Diethyl-¹⁹ and dimethyl-²⁰ magnesium are polymers in the solid state. The only solvated dialkylmagnesium complex containing a neutral Lewis base whose structure has been determined is $(\text{C}_6\text{H}_5\text{C}\equiv\text{C})_2\text{Mg} \cdot 4\text{C}_4\text{H}_8\text{O}$,²¹ a six coordinate monomer.

A crystallographic study of the reaction product of dimethylmagnesium with quinuclidine shows the compound to be a four coordinate disolvated monomer. This study indicates that the stereochemistry about the magnesium atom is dependent upon the steric requirements of the solvent group.

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STUDIES OF TRIETHYLENEDIAMINE COMPLEXES OF RUTHENIUM

Sister Helen Elsbernd

May 15, 1969

Trisethylenediamine complexes are known for many of the transition metals. Some of these, such as those of Cr(III), Co(III), and Pt(IV), have been studied extensively since the beginning of coordination chemistry. The syntheses of trisethylenediamine complexes of ruthenium, however, have been reported only in recent years.^{1,2} Further investigation of these ruthenium complexes was of interest because of the correlations possible with the analogous complexes of other transition metal ions, the various anomalies observed in the properties of these ruthenium complexes, and the fact that trisethylenediamine complexes exist for ruthenium in several oxidation states.

The syntheses of $\text{Ru}(\text{en})_3^{3+}$ and $\text{Ru}(\text{en})_3^{2+}$ ³ and the infrared spectra of several salts of the latter complex⁴ can be found in the literature. $[\text{Ru}(\text{en})_3]\text{ZnCl}_4$ and $[\text{Ru}(\text{en})_3]\text{ZnBr}_4$ are yellow salts with an absorption spectrum consisting of two maxima: $\lambda = 370 \text{ nm}$ ($\epsilon = 120 \pm 10$) and $\lambda = 302$ ($\epsilon = 1020 \pm 60$).² A dilute solution of $\text{Ru}(\text{en})_3^{3+}$ exhibits a maximum only at $\lambda = 310 \text{ nm}$ ($\epsilon = 360 \pm 25$),² yet the solid crystals of $[\text{Ru}(\text{en})_3]\text{I}_3$ are dark purple and $[\text{Ru}(\text{en})_3]\text{Br}_3$ is bright yellow. The intense colors of the crystals are due to charge transfer from the anions in the crystals to the complex cation.⁵ The salts and the ion pair of iodide with $\text{Ru}(\text{en})_3^{3+}$ in solution are striking examples of this outer-sphere charge-transfer phenomenon since the charge-transfer transition is of considerably lower energy than the first d-d transition of the complex.

A brown substance with intense absorption at 448 nm ($\epsilon = 7000$) is obtained from the oxidation of $\text{Ru}(\text{en})_3^{2+}$ in basic medium with iodine. Air oxidation of $\text{Ru}(\text{en})_3^{2+}$ and $\text{Ru}(\text{en})_3^{3+}$ in solution also yields the same product. The formulation of the iodide salt as $[\text{Ru}(\text{en-H})_2\text{en}]\text{I}_2$, where en-H represents a deprotonated ethylenediamine ligand, is supported by the elemental analysis, the determination of the charge per ruthenium atom as +2, its diamagnetic character, and comparisons with the known complex $[\text{Os}(\text{en-H})_2\text{en}]\text{I}_2$.⁶ For example, the molar conductance found for a 10^{-4} M solution of $[\text{Ru}(\text{en-H})_2\text{en}]\text{I}_2$ at 25°C is 255 ohms⁻¹, of $[\text{Os}(\text{en-H})_2\text{en}]\text{I}_2$, 260 ohms⁻¹. Aqueous solutions of this Ru(IV) complex are acidic and are very stable.

The $\text{Ru}(\text{en})_3^{3+}$ ion has been resolved into its optical enantiomers through fractional precipitation with optically active $\text{Rh}(\text{ox})_3^{3-}$.⁷ The circular dichroism (CD) spectrum of $(-)_350\text{-Ru}(\text{en})_3^{3+}$ consists of two bands: $\lambda_{\text{max}} = 284 \text{ nm}$ ($\Delta\epsilon = +2.12$) and 328 nm ($\Delta\epsilon = -0.87$). Reduction of $(-)_350\text{-Ru}(\text{en})_3^{3+}$ with zinc amalgam in an inert atmosphere yields $(-)_375\text{-Ru}(\text{en})_3^{2+}$ with complete retention of optical activity. The $(-)_375\text{-Ru}(\text{en})_3^{2+}$ enantiomer exhibits a CD spectrum with maxima at 284 ($\Delta\epsilon = -2.32$), 348 ($\Delta\epsilon = -1.49$) and 402 nm ($\Delta\epsilon = +0.93$). The optical rotatory dispersion curve for both enantiomers is a complex composite of negative and positive Cotton effects. Both complexes show negligible rotation at the sodium D-line.

The absolute configurations of the enantiomers have been assigned by the methods of least soluble diastereoisomers⁸ and active racemates⁹ for the Ru(III) complex and from the band assignments of the CD spectrum¹⁰ for the Ru(II) complex. Both $(-)_350\text{-Ru}(\text{en})_3^{3+}$ and

$(-)\text{-}_{375}\text{-Ru(en)}_3^{2+}$ were found to have the same configuration as $(+)\text{-Co(en)}_3^{3+}$; that is, the D-configuration.¹¹

The nuclear magnetic resonance spectrum of Ru(en)_3^{2+} is anomalous by comparison with that of other M(en)_3^{n+} complexes. The methylene proton spectrum in the absence of coupling with the amine protons, which can be eliminated by deuteration, consists of a single resonance of only a few cycles width for the Rh(III) ¹² and Pt(IV) complexes and a broad peak of about 18 cycles width for Co(III) .¹³ By contrast, the NMR spectrum of deuterated Ru(en)_3^{2+} is a complex structure, namely, a typical AA'BB' spectrum at both 60 MHz and 100 MHz with the center of the band 2.55 ppm downfield from DSS. In the spectrum of the non-deuterated complex two distinct amine proton resonances can be observed in the region 2.8 to 4.5 ppm downfield from DSS. Quite remarkably the multiplet structure of the methylene protons persists in 0.1 M tri-fluoroacetic acid solution up to 100°C.

The fine structure in the Ru(en)_3^{2+} NMR spectrum arises from the fact that in the conformational isomers possible in chelated ethylenediamine ligands the methylene protons are non-equivalent, assuming approximately axial and equatorial positions.¹⁴ The absence of multiplets in the NMR of the Rh(III) , Co(III) and Pt(IV) complexes has been attributed to rapid conformational interconversion^{12,13} and comparable population of conformational states.¹⁵ The AA'BB' spectrum of Ru(en)_3^{2+} may be due to the ethylenediamine rings being strongly locked in one conformation, or to one conformation being present in a very large excess.¹⁵ Present observations do not allow one to determine whether the observed multiplet structure is due to kinetic or thermodynamic factors.

The methylene resonances of Ru(en)_3^{3+} are observed as a broad band at 12.7 ppm downfield from DSS with a linewidth of about 200 Hz. Addition of small concentrations of Ru(en)_3^{3+} (10^{-3} - 10^{-4} M) to a Ru(en)_3^{2+} solution results in profound changes in the spectrum of the Ru(II) complex. Further investigation into the phenomenon involved in these changes, as well as a complete analysis of the Ru(en)_3^{2+} NMR spectrum, is still in progress.

Attempts have been made to measure the rate of electron exchange between Ru(en)_3^{3+} and Ru(en)_3^{2+} . Meyer and Taube determined $k_{ex} \approx 200$ through a spectrophotometric method in the infrared region, but the study was beset with catalytic problems.³ By following the loss of optical activity when racemic Ru(III) solutions were added to active Ru(II) solutions, or vice versa, exchange constants greater than 10^3 were obtained. To eliminate the possibility of light catalysis, NMR methods were attempted. However, the unexpected complexity of the Ru(en)_3^{2+} spectrum has thus far delayed this kinetic study of the electron exchange phenomenon.

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TABLE OF CONTENTS
INORGANIC SEMINAR ABSTRACTS

1968-1969

Page

COORDINATION NUMBER AND GEOMETRY OF SOME COPPER(II) AMINE COMPLEXES - Walter John Kasowski	1
SUBSTITUTION REACTIONS OF OCTAHEDRAL METAL CARBONYL COMPLEXES - Richard L. Kieft	1
PRODUCTION AND STUDY OF TITANIUM MONOHALIDES BY FLASH HEATING - Robert L. Diebner	2
THEORIES OF BONDING AND STRUCTURE IN TRANSITION METAL SYSTEMS - John B. Callen	9
SOME MAGNETICALLY ANOMALOUS COMPOUNDS OF IRON(II) - Lucille Novak	14
PROTONATION OF ORGANOMETALLIC TRANSITION METAL COMPLEXES - David P. Novak	19
FIVE COORDINATE COMPLEXES OF DIVALENT COBALT - Thomas Maier	22
COBALT-59 NUCLEAR QUADRUPOLE RESONANCE - Raymond S. Stewart	25
STEREOCHEMICALLY NON-RIGID ORGANOMETALLIC MOLECULES - R. Sneath	28
FLASH HEATING AS A TECHNIQUE FOR HIGH TEMPERATURE SPECTROSCOPY - Michael Garrett	33
BIO-INORGANIC SYSTEMS: THE DETERMINATION OF THE CHEMICAL AND STRUCTURAL PROPERTIES OF HEMOGLOBIN - James S. Swanson	30
PHOTOCHEMISTRY OF Cr(III) AND Co(III) INORGANIC COMPLEXES - Robert L. Chiang	33
INFRARED STUDIES OF THE TRANS INFLUENCE IN SQUARE PLANAR COMPLEXES - Mel Memering	38
STRUCTURAL STUDIES OF CHLORO AND AQUOCHLORO COMPLEXES OF NICKEL(II) - Fred Ross	41
SPIN DELOCALIZATION IN SIGMA SYSTEMS - Roger Cramer	43
RELAXATION METHODS IN KINETIC STUDIES - Kathy Myers	44

Table of Contents (continued)	Page
AN INVESTIGATION OF THE CHRONOPOTENTIOMETRIC OXIDATION OF Pt(II) - Sn(II) COMPLEXES - Denis F. DeCraene	48
NOBLE GAS CHEMISTRY - George F. McKnight	50
STUDIES OF THE EFFECTS OF FLASH HEATING ON CATALYTIC SURFACES - W. Ronald Cares	54
ION CYCLOTRON MULTIPLE RESONANCE AND ITS APPLICATION TO THE STUDY OF GAS-PHASE ION-MOLECULE REACTIONS - Eric F. Johnson	59
APPLICATIONS OF THE WOODWARD-HOFFMANN RULES TO TRANSITION METAL CATALYSIS - Joseph J. Brooks	62
NMR STUDY OF PENTAFLUOROPHENYL DERIVATIVES AND ITS APPLICATION TO THE STUDY OF CHEMICAL BONDING IN INORGANIC COMPOUNDS - Lim Yau-Yan	65
STRUCTURAL AND SPECTROSCOPIC STUDIES OF CERTAIN TRANSITION METAL HALIDES - Gary McPherson	69
STRUCTURAL STUDIES OF ORGANOMAGNESIUM COMPOUNDS - Joe D. Toney	71
STUDIES OF TRIETHYLENEDIAMINE COMPLEXES OF RUTHENIUM - Sister Helen Elsbernd	74

COORDINATION NUMBER AND GEOMETRY OF SOME COPPER(II) AMINE COMPLEXES

By Walter John Kasowski

This seminar will be a critical discussion of the following:

- 1) The coordination number of Cu in the complexes of $C(CH_2NH_2)_4$ with $CuCl_2$.¹
- 2) The effect of N-alkyl substitution in the ethylene diamine complexes of $CuBr_2$ and $Cu(ClO_4)_2$.²
- 3) The preparation of five-coordinate Cu(II) complexes by using the ligand bis-(dimethylaminoethyl)-methylanine.³
- 4) The so-called "psuedo-tetrahedral" complex $Cu(Me_4tn)Br_2$ where $Me_4tn = (CH_3)_2N-(CH_2)_3-N(CH_3)_2$.⁴

Common to all these papers is the application of Visible Absorption Spectroscopy to establish the coordination number and geometry of the copper atom. The technique of Visible Absorption Spectroscopy is applicable because the structures of Cu(II) complexes and their absorption spectra are directly related through Crystal Field Theory.^{5,6,7}

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SUBSTITUTION REACTIONS OF OCTAHEDRAL METAL CARBONYL COMPLEXES

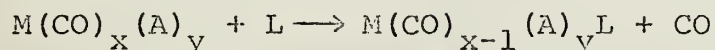
Richard L. Kieft

September 24, 1968

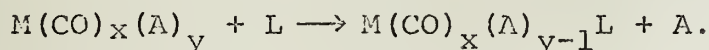
Introduction

Octahedral metal carbonyl complexes undergo substitution₁ reactions with a ligand, L, in two general types of reaction:

1. Replacement of CO,



2. Replacement of another group A,



Recently, the kinetics and mechanism of these two reactions have been studied quite extensively. The kinetics were usually obtained by following the disappearance of the highest frequency carbonyl stretching absorption.₂

Substitution Reactions

A. Hexacarbonyls, $M(CO)_6$

The hexacarbonyls react at temperatures of 100-170°C, and sometimes continue to di- or tri-substitution.₃ Originally this reaction was thought to be a simple first order reaction, but recent work at concentrations of ligand greater than 0.050 molar shows that a two term rate law exists.₄

$$\text{Rate} = K_1[\text{complex}] + K_2[\text{complex}][L].$$

It is immediately obvious that we have two mechanisms operating here. The K_1 term indicates an S_N1 type reaction. This is usually explained in terms of carbonyl dissociation, and formation of a five coordinate intermediate. The K_2 term suggests nucleophilic attack, which is unusual for octahedral complexes.₅ There are two possible mechanisms which could explain this:₃

1. Formation of a seven-coordinate intermediate or activated complex,
2. Attack of the carbonyl carbon.

Seven coordinate complexes of the form $[M(CO)_4X_3]^-$ are known for Cr, Mo, and W, so mechanism 1 is a definite possibility. Attack on the carbonyl carbon is believed to occur only with alkoxide ions,₆ although recent molecular orbital calculations₇ show that the carbonyl carbons do have a slight (+0.25) positive charge and thus might be subject to nucleophilic attack.

B. Pentacarbonyls, $M(CO)_5A$

The pentacarbonyls exhibit a very unusual property of all substituted metal carbonyl complexes: The ability of certain ligands to labilize the remaining carbonyls.⁸ This labilizing ability is exhibited by amines, halides, hydride ion, and nitrates; but is not noticed for phosphines, phosphites, or isocyanides.¹ All the labilizing ligands are "hard" bases,⁹ i.e., good σ donors and poor π acceptors. This effect is probably caused by a destabilization of the ground state, or maybe a stabilization of the transition state.¹⁰

The Group VI B halide pentacarbonyl complexes react according to a two-term rate law,¹ similar to that of the hexacarbonyls, and form $\text{cis-M}(\text{CO})_4\text{LX} + \text{M}(\text{CO})_5\text{L}$. The fact that $\text{cis-M}(\text{CO})_4\text{LX}$ is obtained is generally explained as a result of the increased π bonding to the carbonyl group trans to the halide. The K_2 term is a bimolecular displacement of the halide ion. Group VII B halide pentacarbonyl complexes¹¹ do not cause replacement of the halogen. All halide pentacarbonyls are very reactive, and reactions usually continue until tri-substitution has occurred.

The amine pentacarbonyl complexes react by displacing the amine to form $\text{M}(\text{CO})_5\text{L}$ and $\text{M}(\text{CO})_4\text{L}_2$,¹² or by displacing a carbonyl to form $\text{M}(\text{CO})_4\text{LL}$.¹³

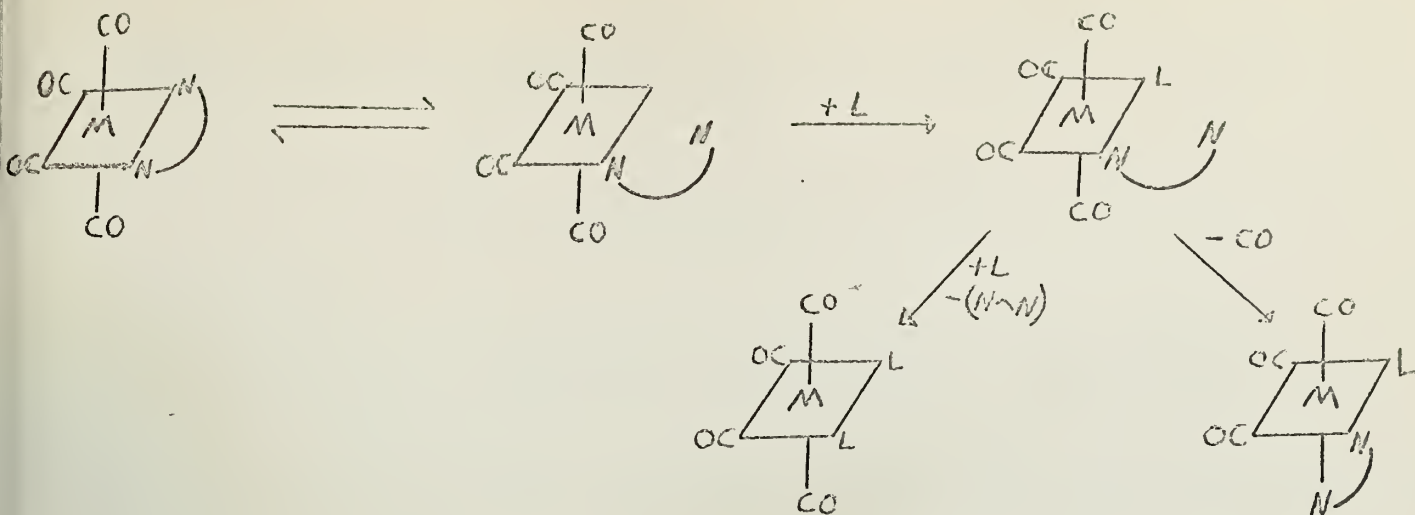
C. Tetracarbonyls, $\text{M}(\text{CO})_4\text{AB}$ ¹⁴

When labilizing ligands are present, these compounds are very reactive, and usually form the tri-substituted product. The cis isomer is formed due to increased π back-bonding to the two carbonyl groups trans to the ligands, making them less susceptible to carbonyl dissociation. In many cases the trans isomers are thermodynamically more stable, due to steric reasons, so a cis-trans isomerization takes place.¹⁵

The group VII B complexes are simple first order reactions with carbonyl dissociation as the slow step.^{16,17} An exception to this is $[\text{Mn}(\text{CO})_4\text{X}_2]^-$ which undergoes a bimolecular reaction. Nucleophilic displacement of a halide ion results in the formation of $\text{Mn}(\text{CO})_4\text{LX}$.

The Group VI B complexes, $[\text{M}(\text{CO})_4\text{LX}]^-$, react similarly, with replacement of a halide ion forming $\text{M}(\text{CO})_4\text{L}_2$.

Some of the most interesting reactions of substituted metal carbonyls are those involving bidentate ligands. Most of this work has been with Group VI B metal carbonyls, in order to work with neutral species. Chromium carbonyls containing a bidentate ligand react differently from the molybdenum and tungsten analogs. With nitrogen bidentates such as o-phenanthroline(o-phen),¹⁸ 2,2'-dipyridyl(dipy),¹⁹ and 1,2-diamino-2-methylpropane(dmp)¹⁹, chromium's small size prohibits nucleophilic attack. Thus it reacts with a simple first order rate, dependent upon carbonyl dissociation, Molybdenum and tungsten^{20,21} have a two term rate law similar to that of the metal hexacarbonyls. The K_1 term involves carbonyl dissociation and is increased as the bidentate basicity is increased. The K_2 term can be nucleophilic attack to form a seven-coordinate intermediate, but a new mechanism can also be operative here.²⁰ This involves the reversible dissociation of half the bidentate ligand:



This mechanism is supported by the fact that $M(CO)_4L_2$ is formed.

Also, the substituted o-phenanthrolines which are too sterically hindered to dissociate in this way, do not form any $M(CO)_4L_2$.

The rate decreases as the bidentate becomes more basic, for the metal becomes less susceptible to nucleophilic attack. A more basic ligand N,N,N',N'-tetramethylethylenediamine, tmen, shows the reversible dissociation of half the bidentate ligand for chromium, $Cr(CO)_4(tmen)$.²²

Recently bidentates with coordinating ligands other than nitrogen have been examined. These include 2,5-dithiahexane, (DTH) which reacts by replacement of the bidentate^{23,10} and 1,2-bis(diphenylphosphino)ethane, (diphos), which is reactive only under drastic conditions to give $(diphos)M(CO)_3L$.² Mixed ligands such as 1-(diphenylphosphino)-2-(diethylamino)ethane, (NP), bis(diethylaminoethyl)phenylphosphine, (NPN); and bis(diphenylphosphinoethyl)ethylamine, (PNP), are also being studied,²⁴ but as yet, rate data are not available.

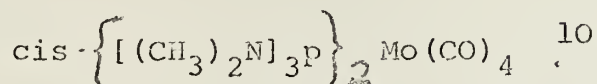
D. Tricarbonyls, $M(CO)_3ABC$

These compounds are generally unreactive, for the carbonyls are very tightly bound. Strong bases are able to replace ligands which are not tightly bound.²⁵ The reactions are simple first order dissociative processes. Also, under drastic conditions, some ligands which are excellent σ and π electron acceptors can replace a carbonyl group. PF_3 , a better π acceptor than carbonyl, can even replace all of the carbonyls.²⁶

Conclusions

Further work is necessary to elucidate the nature of the bonding in octahedral metal carbonyls. A thorough understanding of the carbonyls would be helpful because these compounds are very

useful in synthetic inorganic chemistry, especially in the preparation of new compounds such as



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PRODUCTION AND STUDY OF TITANIUM MONOCHALIDES BY FLASH HEATING ¹

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October 8, 1968

Introduction

There has been considerable interest in the spectra and bonding of diatomic molecules containing transition metals. These molecules are of importance in high temperature chemistry because of their pertinence to studies of the thermodynamics of vaporization processes and equilibria in vapor systems. ^{2,3} A comprehensive review of the spectra of the transition metal diatomics has recently been given by Cheetham and Barrow. ⁴

The use of flash techniques for obtaining large vapor populations for transient species allows absorption spectra to be obtained rather easily. Specifically, Nelson and co-workers ⁵ and Kay and co-workers ^{6,7} have demonstrated the application of flash heating and kinetic spectroscopy to obtain electronic absorption spectra of FeO(g) from metallic iron and oxygen ⁵ and MnO(g) from crystalline KMnO_4 . ^{6,7}

In the work to be discussed, the studies of the effects of flash heating have been extended to the investigation of powdered titanium salts.

Experimental Results

$\text{TiCl}_3(\text{s})$ has been flash heated and absorption spectra of vaporized TiCl obtained. The flash heating of $\text{Na}_2\text{TiCl}_4(\text{s})$ produced similar spectra. The only titanium monohalide spectrum for which data have been reported, prior to this work, is for TiCl(g) , seen in emission ^{8,9} and in absorption by shock-heating gaseous TiCl_4 . ¹⁰

We have obtained and identified the spectrum of TiF(g) , prepared in an analogous way from the flash heating of $\text{TiF}_3(\text{s})$. The same spectrum was obtained from the flashing of $\text{Ti(s)} + \text{SF}_6(\text{g})$, $\text{Ti(s)} + \text{CF}_4(\text{g})$, and $\text{TiF}_4(\text{s})$, with only one band system of TiF being obtained from the flashing of $\text{Ti(s)} + \text{Al}_2\text{F}_6 \cdot x\text{H}_2\text{O(s)}$. No details of the TiF spectrum have been reported in the literature up to this time. The TiF spectrum consists of three different band systems: the main system appears in the region $3930 - 4088\text{\AA}$, with the other systems at $3855 - 3906\text{\AA}$ and $3646 - 3711\text{\AA}$.

Most of the experiments performed utilized a 1.5 meter grating spectrograph having a reciprocal linear dispersion of $5.4\text{\AA}/\text{mm}$ in the region of interest. High-dispersion spectra of TiF(g) and TiCl(g) were obtained using the 30 ft. grating spectrograph at Argonne National Laboratory. This instrument has a reciprocal linear dispersion of $0.9\text{\AA}/\text{mm}$ in the region of interest.

Mass-spectrometric work has also been carried out on flash heated $\text{TiF}_3(\text{s})$. Flashing $\text{TiF}_3(\text{s})$ directly into a time-of-flight mass spectrometer gave further support to the identification of TiF(g) . The results of this work differed somewhat from those of Zmbov and Margrave ³, using Knudsen cell equilibrium techniques.

Vibrational Analysis

A vibrational analysis was carried out on the high-dispersion spectrum of the main TiF system (3930 - 4088 $\overset{\circ}{\text{A}}$). This system is a $\Delta v=0$ sequence; the ground electronic state is found to be ${}^4\Sigma^- (\delta^2\sigma)$ with the upper state for this transition being ($\delta^2\pi^*$ or $\delta\sigma\pi^*$)

The $\Delta v=0$ sequence of $\text{TiCl}(\text{g})$ has also been classified as a ${}^4\Pi-X {}^4\Sigma^-$ transition, ^{8,9} and the similarity is evident when our spectra of TiCl and TiF are compared. Too few bands were observed for the other TiF systems to make an analysis feasible.

Molecular Orbital Description

Only in the last few years has a serious theoretical investigation of transition metal diatomics been undertaken, starting with the crystal field approach of Berg and Sinanoglu. ¹¹ Since that time several molecular orbital calculations and discussions ¹²⁻¹⁴ have been given on such molecules.

As a result of our analysis, the ground state electronic configuration of $\text{TiF}(\text{g})$, has been established as ${}^4\Sigma^- (\delta^2\sigma)$. The ab initio calculations by Carlson and Moser ¹⁵ have predicted for VO, a molecule isoelectronic with TiF, a ground state configuration ${}^4\Sigma^- (\delta^2\sigma)$ also. This prediction has been confirmed by recent ESR studies on VO by Kasai. ¹⁶

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THEORIES OF BONDING AND STRUCTURE IN TRANSITION METAL SYSTEMS

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October 22, 1968

Introduction

During the last two decades there has been a tremendous emphasis placed on the chemistry of systems containing metal-metal bonds--running the gamut from metals themselves to intermetallic compounds and distinct phases to concentrated metal compounds and poly- and hetero-polynuclear complexes. This is primarily due to recent advances in our understanding of the metallic state which has stemmed largely from crystal structures and spectroscopic data.

For many years the study of bonding and interaction in metal systems received little attention from chemists; perhaps part of the reason is due to the fact that many of these systems do not display constancy of chemical composition or conform to principles of chemical valence as we know them. Consequently, it would be important for us to consider these questions of metal chemistry since major contradictions in the understanding of physico-chemical principles have always existed. Because of the broad area this field covers, discussion will be limited to theories of bonding and structure of transition metal systems in categories I and IVc below:

Substances Containing Metal-Metal Bonds¹

- I. Metals and Alloys
 - a. Metals, e.g. Cu
 - b. True alloys, e.g. Cu/Zn
 - c. Salt-like Alloys, e.g. Cs^+Au^-
- II. Concentrated Metal Compounds

e.g. early transition metal compounds of low oxidation state such as MoCl_2
- III. Metal Donor Compounds
 - a. \underline{s}^* donor, e.g. $[\text{Pt}(\text{SnCl}_3)_4]^{3-}$
 - b. \underline{d} donor, e.g. Ni(II) dimethylglyoxime
- IV. Covalent (?) Bond Type
 - a. $\underline{s}^*/\underline{s}^*$, e.g. Hg_2Cl_2
 - b. $\underline{s}^*/\underline{d}$, e.g. $\text{P} \longrightarrow \text{AuMn}(\text{CO})_5$
 - c. $\underline{d}/\underline{d}$, e.g., $\text{Mn}_2(\text{CO})_{10}$

*strictly $\underline{s}/\underline{p}$

Theories of Bonding and Structure

The topic of electronic structure of metals, in particular transition metals, is of great interest from both a theoretical and practical point of view. Moreover, in spite of vast studies made in this field, the question is by no means settled. Up to the present time it has not been quite clear which of the two approximate theories of metallic bonding should be applied to real metals--whether the free electron theory of Mott and Jones and all of its ramifications²⁻⁶ along

with the band model treatment of Bloch and others⁷ or the covalent bond theory of Pauling.^{8,9}

Free electron theory provides a good model and interpretation of many aspects of metallic behavior but cannot be a true theory of metals because all it treats is the kinetic energy of electrons. This theory is structureless and has little to say about the chemical nature of the metallic bond. Cellular models,¹⁰⁻¹² the theory of Brillouin Zones¹³ and band theory of solids prove inadequate for the discussion of the transition metals or can only treat transition metals with many generalizations, although they may account for many of the physical characteristics of metals.

The nature of the chemical bond in the metallic state as a multiplicity of resonating covalent bonds was described by Pauling in 1938.^{8,9} It was based on the fact that by a simple equation

$$D(n) = D(1) - 0.6 \log n \quad (1)$$

for the dependence of interatomic distance D (bond length) on the number n of electron pairs in a bond, he could relate in a consistent way the similarity between covalent and metallic radii. This empirical correlation of Pauling suggests that metallic bond distances increase as the metallic valences increase; this is in agreement with experience. His concept of the metallic bond is useful in interpreting strength, ductility, malleability, and electrical conductivity of metals as well. Yet, the best chemically it can do is to correlate in a consistent way inter-nuclear distances in metals and intermetallic compounds in known structures and relate them to bond distances of the same elements in non-metallic compounds. The viewpoint that there is essentially no difference between the metallic bond and the covalent bond is incorrect; much higher coordination numbers are found in metal crystals than in normal covalent crystals.

The Engel Correlation

Nearly two decades ago Niels Engel¹⁴⁻¹⁷ proposed that for transition metals the body centered cubic (bcc) structure is to be correlated with an electron configuration approximating the configuration $d^{n-1}s$, the hexagonal closest packed (hcp) structure is to be correlated with an electron configuration approximating $d^{n-2}sp$, and the face centered cubic (cubic closest packed-ccp) structure is to be correlated with an electron configuration approximating $d^{n-3}sp^2$. At the time, this theory was not well accepted but a tremendous surge in experimental data, has substantiated his theory. In closed form the theory states that the structure and electron concentration of metals is clearly correlated to the total number of s,p -valence electrons per atom. Why is the structure determined only by the s,p electrons and not the d -electrons if we consider transition metals? We find out that the d -electrons play an important role in determining the structure indirectly; once the d -electrons have determined the promotion and bond energies from the ground to excited states, then the crystal structure is fixed by the concentration of the remaining s,p -electrons. Consequently, the Engel Correlation can be used as a more quantitative means to allow prediction of

thermodynamic properties of bcc and hcp structures even when they are not observed for the pure element. It can explain reasons for the increase in bonding strength of d-electrons from the first to third transition series, predict the effect of pressure on the relative stabilities of different crystal structures of transition metals and leads to an understanding of the limited occurrence of ferromagnetism in these metals. It can also characterize their optimum electron configuration.¹⁹⁻²³

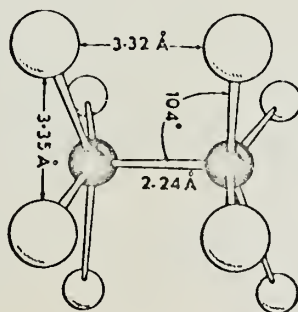
Metal Cluster Systems

It has been only recently that chemists have become increasingly aware of the general importance of metal-metal bonding in transition metal polynuclear systems. As has been previously implied, it is the direct overlap of transition metal d-orbitals that is responsible for strong metal-metal bonds. One should, however, distinguish between criteria for the existence of a metal-metal bond as opposed to a metal-metal interaction which amounts to only a pairing of electron spins sufficient to lessen or quench paramagnetism. Neutron diffraction can distinguish these two cases but at present is not in common use. Perhaps the most useful criterion is that of structural characteristics of the molecule although these data are not necessarily conclusive.

With respect to crystal structures, two useful criteria for interpretation of the existence of metal-metal bonds have been proposed.²⁴⁻²⁷

1. When there are adjacent metal atoms with no bridging groups metal-metal bonds must obviously exist; and,
2. When there are also bridging groups, for example, halides or carboxylate ions, a metal-metal bond is said to exist if metal atoms approach each other more closely than the bridging geometry would appear to require. If the metal distance is a relatively long one, which does not differ significantly from what would be expected in the absence of any direct attractive force between metal atoms, we assume that nothing more than weak spin coupling is involved.

In order to explain the structural features of $[\text{Re}_2\text{Cl}_8]^{2-}$ and the nature of the Re-Re bond, Cotton uses extended Hückel molecular orbital theory.^{28,29} The calculations infer that the π -bonding contribution to the Re-Re bond is five times that of the δ -bonding and three times that of the σ -bonding. Although it is evidently the weakest of the Re-Re bonds, the δ -bonds are of greatest importance. The σ -bond and the pair of π -bonds have strengths which are independent of the angle of internal rotation between the two ReCl_4 units of the following structure:³⁰



The structure of
the $\text{Re}_2\text{Cl}_8^{2-}$ ion, as found in
 $\text{K}_2\text{Re}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$

but the σ -bond is sensitive to this angle. The presence of δ -bonds provides an explanation for the occurrence of the eclipsed configuration since in the staggered configuration the overlap would be zero and the δ -bond would be non-existent. Despite this particularly pleasing interpretation, extended Hückel theory is far from satisfactory in interpreting the spectrum for both electric dipole allowed and vibronically induced transitions.

Conclusions

Although the Engel Correlation and Cotton's interpretations provide new insight into interpretation of metal-metal bonding, it is apparent that further work in the field of metal chemistry is needed to provide a sound theory of the nature of the chemical bond in the metallic state.

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SOME MAGNETICALLY ANOMALOUS COMPOUNDS OF IRON(II)

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October 29, 1968

Introduction

Usually octahedral transition metal coordination compounds exist in one of two electronic ground states, referred to as high-spin and low-spin configurations, which depends upon the strength of the ligand field. However, in recent years, a number of octahedral iron and cobalt compounds have been discovered in which the high- and low-spin ground states have approximately the same energy and thus the electrons exist in an equilibrium between the two configurations.^{1,2,3} This phenomenon results in an anomalous magnetic behavior which is markedly temperature dependent.

Theory

In octahedrally coordinated iron(II), the ground states for the high- and low-spin configurations are $^5T_{2g}$ and $^1A_{1g}$, respectively. Examples of the normal magnetic behavior for iron(II) compounds are shown below.

Table 1.

number of unpaired e ⁻	ground state	compound	$\frac{\mu_{so}}{\sqrt{4S(S+1)}} =$ B.M.	T°K	μ_{eff} ^{4,5} B.M.
0	1A_1	[Fe(phen) ₂ (CN) ₂]	0.0	289	~0
4	5T_2	[Fe(phen) ₂ Cl ₂]	4.90	291	5.27

There is no first order Zeeman effect on the singlet state; however, the second order Zeeman effect produces a slight positive susceptibility in some compounds.⁶ The moment is temperature independent.

For the quintet state, the magnetic moment calculated using a spin-orbit coupling term of $\lambda \approx 100 \text{ cm}^{-1}$ is 5.6 B.M. at 300°K. The effective magnetic moment is reduced from this because the actual symmetry field is lower than O_h .⁵

In some cases, when the ligand field is of medium strength, the ground states of the high- and low-spin configurations have approximately the same energy. If the separation between the two states is of the order of kT, thermal equilibrium between the two states will exist. In such cases the populations of the two terms will vary with temperature, and the magnetic susceptibility will be a population-weighted average of the susceptibilities of the two ground states. The condition for the existence of spin equilibrium is:
 $\Delta_{H.S.} < \pi < \Delta_{L.S.}$,¹⁰ where $\Delta_{H.S.}$ = high-spin ligand field splitting, $\Delta_{L.S.}$ = low-spin ligand field splitting, and π = mean spin pairing energy.

The magnetic behavior of the iron(II) salts has been extensively studied, and two distinct classes of anomalous compounds are recognized--those existing in a thermal spin equilibrium (Class I), and those showing anomalous temperature dependence but exhibiting a sharp transition from a high- to a low-spin ground state at a distinct temperature (Class II).

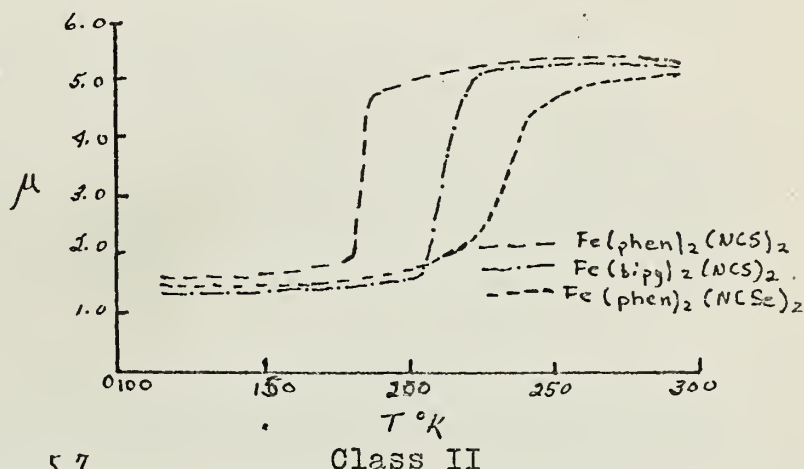
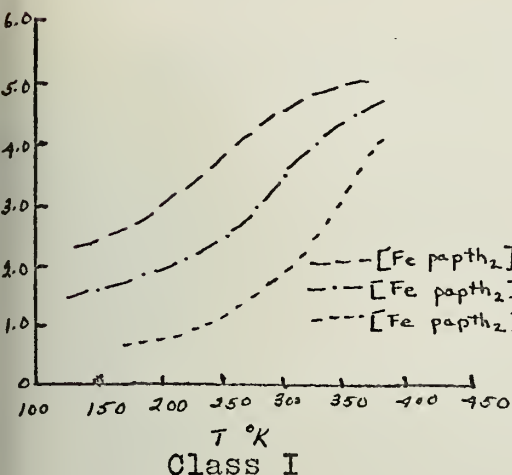


Figure 1.

Class I Compounds

Sylva and Goodwin report that [bis(2-(2-pyridylamine)-4-(2-pyridyl)thiazole)iron(II)]X₂ and [tris(2-methyl-1,10-phenanthroline)iron(II)]X₂, [Fe(papth)₂]X₂ and [Fe(mephen)₃]X₂, respectively, exist in spin equilibrium.^{7,8,9} At 400°K they are in a high-spin state and at 200°K, a low-spin state. In both compounds the magnetic moments vary continuously from high- to low-spin (cf. Figure 1.), and the behavior is reversible.

X was varied over a number of anions. The magnetic behavior is markedly dependent on the anion used and the number of waters of hydration present. Anomalous behavior is observed when X = NCS, Br, Cl, or NO₃.

Quantitative fit of magnetic data using the Van Vleck equation is not successful since no unique determination of the molecular parameters can be made. However, an equilibrium constant can be defined.

$$\text{spin paired} \rightleftharpoons \text{spin free} \quad K = \frac{[\text{SF}]}{[\text{SP}]}$$

A plot of log K versus 1/T is curved, indicating that the magnetic changeover is not a function of a single value of ΔH. The temperature dependence of ΔH indicates a change in the heat capacity of the system which could reflect a change in the crystal lattice due to a change in the metal-ligand bond length.¹⁰

In addition to causing anomalous magnetic behavior, spin equilibrium should result in a temperature dependence of the visible spectra. This was found to be true by observing the color changes of the salts upon cooling.

Class II Compounds

Magnetic Data

Baker and coworkers, and König and Madeja have studied the magnetic behavior of [bis(1,10-phenanthroline) iron(II) X_2]-[Fe(phen) $_2X_2$].^{4,5,11} Again, the magnetic behavior is dependent upon the anion used; however, in this case, the anion is in the coordination sphere. If $X = Cl^-$, Br^- , I^- , N_3^- , OCN^- , $HCOO^-$, or CH_3COO^- , high-spin compounds are formed. If $X = CN^-$, CNO^- , or NO_2^- , diamagnetic compounds are formed. Anomalous magnetic behavior is observed when $X = NCS$ and NCS^- . The magnetic moments of the thiocyanate and selenocyanate drop sharply from ~ 5.0 B.M. to ~ 1.5 B.M. at critical temperatures of $174^\circ K$ and $232^\circ K$, respectively (cf. Figure 1.).

The magnetic behavior of these compounds depends upon the method of preparation. At least two polymorphs were studied. The polymorphs have the same Mössbauer, electronic and infrared spectra but differ in crystal structure.

X-Ray Data

Powder photographs were taken at both 298 and $77^\circ K$. There is no phase change.

Mössbauer Data

Mössbauer spectra were measured at 293 and $77^\circ K$. Data for some of the compounds are given below.

compound	$T^\circ K$	11,12 Table 2.		
		ground state	δ mm/sec	ΔE_Q mm/sec
Fe(phen) $_2(NCS)_2$	293	$^5T_{2g}$	0.98	2.67
	77	$^1A_{1g}$	0.37	0.34
Fe(phen) $_2(NCSe)_2$	293	$^5T_{2g}$	1.03	2.52
	77	$^1A_{1g}$	0.35	0.18
Fe(phen) $_2Cl_2$	293	$^5T_{2g}$	0.96	3.00
	77	$^5T_{2g}$	~ 0.96	~ 3.00
Fe(phen) $_2(NO_2)_2$	293	$^1A_{1g}$	0.28	0.38
	77	$^1A_{1g}$	~ 0.28	~ 0.38

The isomer shift, δ , measures the total s-electron density at the nucleus. Since the $^1A_{1g}$ state can more effectively back-bond to vacant π^* ligand orbitals, the larger electron delocalization in the $^1A_{1g}$ state causes a decrease in the shielding of the core s-electrons, and δ will be larger for the $^5T_{2g}$ than for the $^1A_{1g}$ ground state.¹³

The quadrupole splitting, ΔE_q , arises from the interaction of the ^{57}Fe nuclear quadrupole moment, Q , with the electric field gradient about the nucleus. Thus, ΔE_q will be larger for the non-spherically symmetric $^5\text{T}_{2g}$ state than for the spherically symmetric $^1\text{A}_{1g}$ state.

Infrared Spectra

The infrared spectra show that the thiocyanate and selenocyanate bonding occurs through the nitrogen.¹¹ The C-N stretching mode, ν_1 , shifts from 2116 to 2103 cm^{-1} ($^5\text{T}_{2g} \rightarrow ^1\text{A}_{1g}$). This is in accord with an increase in back-bonding from the metal to the π^* phenanthroline orbital in the $^1\text{A}_{1g}$ state. The higher availability of $^1\text{A}_{1g}$ electrons decreases the strength of the metal-N bond and thus increases the C-N bond. It has also been found that the intensity of ν_1 shows essentially the same temperature dependence as the magnetic moment.¹⁴ The N-C-S bend, ν_2 , and the C-S stretch, ν_3 , are not changed by the transition.

An analysis of the characteristic phenanthroline frequencies is more difficult. König and Madeja observed that the conjugation of the π -electrons in phenanthroline is diminished on going from the quintet to the singlet state--as would be expected since the π^* -metal back-bonding increases.¹⁵

Electronic Spectra

The electronic spectra of these compounds are not easy to interpret since (1) it is not possible to find the value of $10 Dq$ directly from the spectra in the low-spin case, and (2) band assignments are difficult.^{11,10}

Bis-dipyridyl compounds

2,2'-dipyridyl forms an analogous series of bis-compounds with iron(II). Again, the NCS^- and NCSe^- compounds are magnetically anomalous. These compounds show the same type of magnetic behavior and spectra as do the bis-phenanthroline compounds.¹⁷

Conclusions

The spectral and magnetic data demonstrate qualitatively that above the critical temperature these compounds exist in a $^5\text{T}_{2g}$ ground state and below this temperature they exist in a $^1\text{A}_{1g}$ ground state. However, quantitative agreement with theoretical equations for thermal equilibrium and magnetic susceptibilities is poor. One explanation for this is that non-equilibrium conditions are involved.¹¹ The two electron change from $t_{2g}^6 \rightarrow t_{2g}^4 e_g^2$ should be followed by an increase in the ionic radius of $\sim 0.2 \text{ \AA}$,¹⁸ which will cause crystalline modifications and alter the environment of the metal. Further investigations, including detailed crystallographic studies should help to explain this phenomenon.

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PROTONATION OF ORGANOMETALLIC TRANSITION METAL COMPLEXES

David P. Novak

November 5, 1968

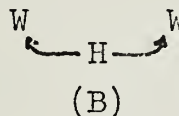
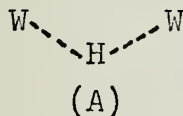
Introduction

The protonation of different organometallic transition metal complexes containing π -bonded organic ligands can produce some interesting cations. Protonation sometimes results in a complex with the proton bonded to the metal, sometimes in a complex with the proton bonded to the ligand, and sometimes in a complex with the proton shared by both the metal and the ligand. The purpose of this seminar is to discuss some of the factors which may influence the site of protonation.

Protonation on the Metal

When complexes containing a metal atom π -bonded to two cyclopentadienyl rings are placed in strongly acidic solutions, a high field proton resonance characteristic of a metal-hydrogen bond is observed. Ferrocene, ruthenocene, and osmocene are protonated in this manner in solutions of boron trifluoride hydrate, ($\text{BF}_3 \cdot \text{H}_2\text{O}$). Di- π -cyclopentadienyl hydrides of rhenium, molybdenum, and tungsten can likewise be protonated on the metal by dilute mineral acids or trifluoroacetic acid.¹ All of these complexes are isoelectronic, containing 18 electrons in the valence shell of the metal. X-ray crystal structure studies of $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ show a non-linear metal-to-ring axis. Molecular orbital calculations by Ballhausen and Dahl,² as well as spectroscopic evidence, support similar non-linear structures for the other di- π -cyclopentadienyl complexes.

Several binuclear π -cyclopentadienyl metal carbonyls, e.g., $[\text{C}_5\text{H}_5\text{M}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}, \text{W}$), are also protonated in strongly acid solutions. High resolution proton resonance spectra of these solutions show that the proton is associated with both of the metal atoms in the binuclear complex. However, whether the proton is equidistant from the metal as in the static model (A) or whether it is undergoing rapid intramolecular exchange between the two metal atoms as in model (B) cannot be determined from the ^1H nmr spectra.¹

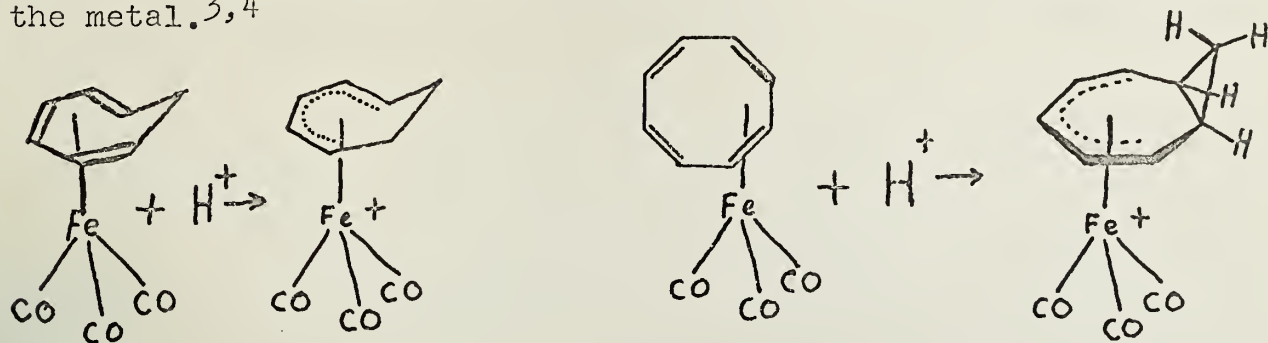


The metal can also be protonated in many mononuclear π -cyclopentadienyl metal carbonyls and arene metal carbonyls. For example, $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$, $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$, and $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ have been studied in strongly acidic solutions.¹

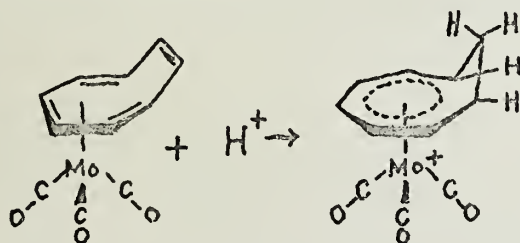
Protonation of the Ligand

When certain transition metal carbonyls which contain a π -bonded olefin as a ligand are placed in strong acid, protonation is found to occur on the π -bonded ligand. Wilkinson, et. al., have studied the

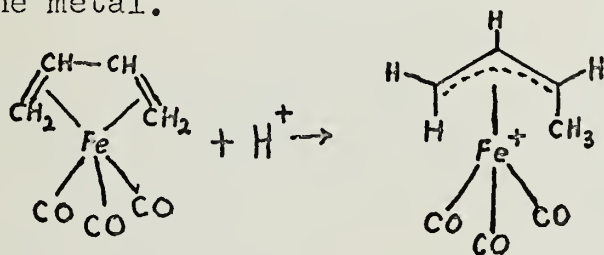
protonation of olefin iron tricarbonyl complexes. These complexes contain a ligand with a double bond which is not coordinated with the metal.^{3,4}



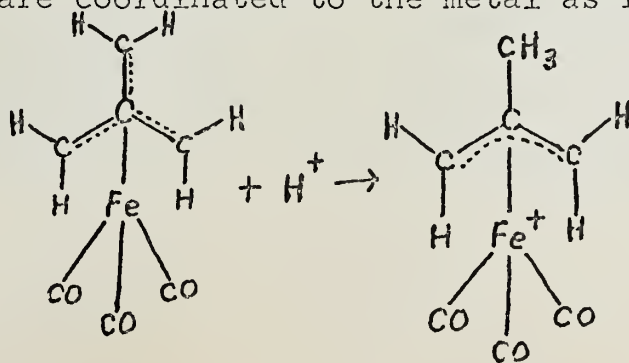
Winstein and co-workers have studied the protonation of cyclo-octatetraene molybdenum tricarbonyl. They concluded that the proton added to the ring as with $C_8H_8Fe(CO)_3$, but that in this case the carbonium ion formed was a monohomotropilium ion instead of the bicyclo-[5,1,0]octadienium ion as in the iron analog.^{5,6}



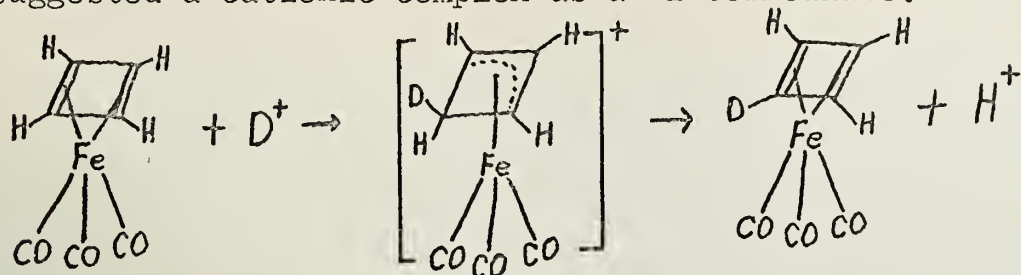
Pettit has recently found that butadiene-iron tricarbonyl can be protonated in strong acid.⁷ In this case, the double bond already involved in coordination to the metal is protonated. This is contrary to work by Wilkinson in which the same compound was reported to be protonated at the metal.



The unusual complex trimethylenemethaneiron tricarbonyl has also been protonated on the ligand.⁸ In trimethylenemethane, the π -orbitals on the ligand are coordinated to the metal as in butadiene-iron tricarbonyl.



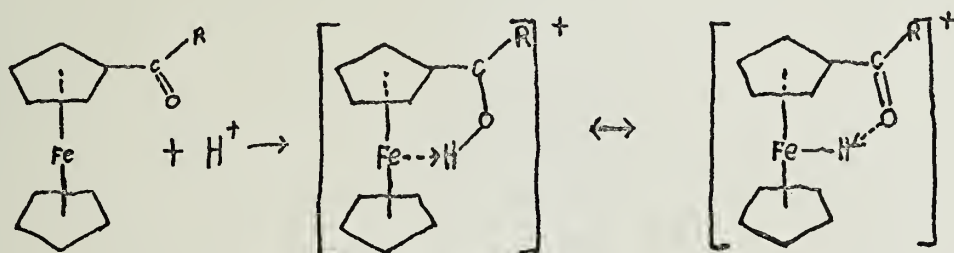
Pettit has found that cyclobutadiene-iron tricarbonyl undergoes electrophilic substitution under very mild conditions to give a variety of monosubstituted cyclobutadiene-iron tricarbonyls. He has suggested a cationic complex as an intermediate.⁹



This would be another case of attack on a π -bonded ligand by a cationic species.

Protonation "between" the metal and the ligand

Several acylferrocenes are reversibly protonated by gaseous HCl. Spectroscopic evidence indicates that an intra-molecular hydrogen bond is formed between the metal and the oxygen.¹



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FIVE COORDINATE COMPLEXES OF DIVALENT COBALT

Thomas Maier

November 12, 1968

Although five coordinate Co(II) complexes have been reported for almost two decades, there is reason to believe that many of the early complexes were not five coordinate.¹ More recently, however, both high- and low-spin five coordinate complexes of Co(II) have been prepared and characterized. In general, these complexes are neither square pyramidal nor trigonal bipyramidal, but are distorted from these two idealized structures. Many different methods have been used to establish the exact nature of these complexes. These methods include conductivity measurements, absorption and reflectance spectroscopy, electron spin resonance, magnetic susceptibility, and x-ray crystallography. Both high-spin and low-spin complexes have been studied.

Sacconi, Ciampolini, and co-workers have done most of the work with the high-spin complexes. Linear, non-bulky, polyamines, such as ethylenediamine,² diethylenetriamine,³ and triethylene-tetramine,⁴ form six coordinate complexes. Bulkier polyamines, such as bis(2-dimethylaminoethyl)methylamine,⁵ bis(2-diethylaminoethyl)amine,⁵ tris(2-aminoethyl)amine,⁴ and tris(2-dimethylaminoethyl)amine,⁶ form five coordinate complexes. X-ray crystallography has shown these complexes to have structures ranging from trigonal bipyramidal (essentially C_{3v} symmetry) to distorted square pyramidal (distorted C_{4v} symmetry). Gillespie⁷ has discussed both idealized structures from electrostatic interactions and has concluded that the trigonal bipyramidal structure would be favored in complexes with a large amount of "covalent character" and the square pyramidal structure would be favored in complexes with a large amount of "ionic character." However, in the solid state the structures of these five coordinate complexes of Co(II) seem to be determined mainly by steric requirements.

In non-coordinating solvents, conductivity and molecular weight studies have shown that although there is some (up to approximately 10%) dimerization, in general the complexes are monomeric. The most convincing evidence for the structure of the complexes in solution has come from visible and ultraviolet absorption spectroscopy. Ciampolini⁸ has been able to fit the observed spectra (which are significantly different from the spectra of either tetrahedral or octahedral Co(II) complexes⁹) of some complexes to a crystal field theory calculation assuming five equivalent point dipoles in a trigonal bipyramidal arrangement (strictly D_{3h} symmetry). Because of some discrepancies in the observed and calculated spectra, Wood¹⁰ performed a crystal field calculation assuming point charges in D_{3h} symmetry. Qualitatively this energy level diagram is similar to that of Ciampolini, but there are several small differences which lead to a slightly different assignment of bands. In either case, the observed spectra

are a good indication of the presence of five coordinate complexes in solution. Absorption spectroscopy has also been used to show the presence of an equilibrium between five and six coordinate structures in solution when the ligand was tris(2-aminoethyl)amine.

Additional information concerning conditions necessary for five coordinate high-spin complexes has come from a study of Schiff bases formed from salicylaldehydes (and related compounds) and N,N-substituted ethylenediamines.^{11,12} Depending on exact nature of the ligand, the coordination number can be six, five, or four. For the five coordinate complexes, structures range from trigonal bipyramidal to distorted square pyramidal.

From a consideration of these ligands which do form five coordinate complexes, several rules for high-spin five coordination can be given:

- 1) Ligand must be multidentate;
- 2) Ligand must be sufficiently bulky to prevent six-coordination;
- 3) Donor atoms must possess strong coordinating ability so five-coordination is achieved;
- 4) Many of the donor atoms must be highly electro-negative, so bonds are mainly "ionic";
- 5) π -bonding ability must be weak.

Although the low-spin five-coordinate complexes were discovered before the high-spin complexes, less work has been done with the low-spin complexes. Venanzi and co-workers¹³ have been able to fit the visible and ultraviolet spectrum of $[\text{Co}(\text{NO}_2)(\text{QP})]^+$ (QP = tris(o-diphenylphosphinophenyl)phosphine) to his ligand field calculation for D_{3h} symmetry. A recently prepared complex of Co(II) with tris(2-diphenylphosphinoethyl)amine¹⁴ with iodide or thiocyanate as anion is also low-spin and qualitatively fits the energy level diagram of Venanzi.

Two additional complexes of Co(II) with five cyanide¹⁵ or methyl isocyanide¹⁶ ligands have been prepared recently. These low-spin complexes have been prepared recently. These low-spin complexes have been studied by electron spin resonance at both 77°K and 300°K in ethylene glycol. These complexes are assumed to be of C_{4v} symmetry based on a comparison of g_{11} and g_1 with those predicted for C_{4v} and D_{3h} symmetry. Also, the visible and ultraviolet absorption spectrum can be explained qualitatively by the d-orbital splitting expected for a square pyramidal structure. Electron spin resonance indicates that with excess methyl isocyanide a six coordinate complex is formed.

Although the magnetic moment of a complex has been used as an indication of slight distortions from octahedral or tetrahedral symmetry, very little work has been done to correlate five coordinate structures with magnetic moment. Most often the magnetic moment is measured only to classify the complex as "high-spin" or "low-spin." For "low-spin" complexes,¹⁴ the magnetic moments have been found to

fall in the range 1.9 to 2.5 B.M. This is higher than the spin-only value of 1.73 B.M., so there must be some orbital contribution. These values are also intermediate between those of octahedral symmetry (1.8-2.0 B.M.) and square planar (2.3-2.9 B.M.). For "high-spin" complexes, the magnetic moments are found in the range 4.1 to 4.8 B.M., considerably higher than the spin-only value of 3.88 B.M. Of these values, the lower moments may be due to the presence of some Co(III) since in solution Co(II) is easily oxidized to Co(III) by oxygen. From a study of magnetic moments at temperatures from 77°K to 300°K, the contribution from second-order Zeeman terms (TIP) is found to be small and the higher value must come from an orbital contribution due to a mixing of ground (4A_2) and higher (primarily 4E) terms under spin-orbit coupling.⁵

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COBALT-59 NUCLEAR QUADRUPOLE RESONANCE

Raymond S. Stewart

November 19, 1968

Introduction:

The purpose of this seminar is to examine some recent studies of inorganic compounds utilizing Co-59 nuclear quadrupole resonance (NQR). The principles and instrumentation of NQR have been reviewed by several authors.¹⁻⁴ Furthermore, a general introduction to the NQR technique was the subject of a seminar by Carlson.⁵ Therefore, the theory outlined in this seminar will be limited generally to the Co-59 nucleus.

Theory:

The NQR phenomenon is one in which radiofrequency energy is absorbed due to the interaction of the quadrupole moment of a nucleus with an asymmetric charge distribution surrounding the nucleus. Only nuclei having a spin angular momentum greater than one-half will have a quadrupole moment, Q . Q is a measure of the deviation of the charge distribution of the nucleus from spherical symmetry.

If a quadrupolar nucleus is located at the origin of a coordinate system and is surrounded by a collection of charges, q_i , the nucleus will experience an electrostatic potential, V , and an electric field, E . The change in the electric field with respect to one of the coordinate axes is the component of the electric field gradient along that axis. In general, the electric field gradient, q , can be written as a tensor containing nine components. A so-called "principal axis system" is introduced to diagonalize q . For an interaction to occur between the quadrupolar nucleus and the charge distribution surrounding it, at least two of the three components of the field gradient along the x , y , and z axes of the principal axis system must be unequal to each other. When all three components are unequal to each other, an asymmetry parameter, η , is introduced. For axially symmetric cases, $\eta = 0$.

Other parameters of interest are α , β , and γ , Eulerian angles which relate the principal axis system to other axis systems. Although these angles are relevant for single crystal studies, polycrystalline samples require only q and η to describe the field gradient.

The quantized energy states depend on the nuclear spin quantum number, I , for the particular quadrupolar nucleus of concern. For the Co-59 nucleus, $I = 7/2$. There would then be three observable transitions in the absence of an external magnetic field and their magnitude would be on the order of megaHertz.

There are three general contributions to the field gradient:

- (1) Inner orbital electrons in the atom containing the quadrupolar nucleus;
- (2) Valence electrons of the atom in question plus electrons involved in the bond or bonds between the atom containing the quadrupolar nucleus and the rest of the molecule;
- (3) Electrons in other parts of the molecule and in other ions in the lattice.

Applications:

Harris⁶ examined the pure Co-59 NQR spectrum of $\text{Cs}(1,2\text{-B}_9\text{C}_2\text{H}_{11})_2\text{Co}$ to obtain information about similarities and differences between π -cyclopentadienyl-metal and π -carborane-metal bonds. Although an X-ray diffraction study had been done by Zalkin, et al.,⁷ on the compound, the carbon atoms were found to be disordered and it was therefore impossible to say whether or not the carbon atoms were adjacent in each molecule and if the crystal contained a single isomer or more than one isomer. Consequently, the NQR study was undertaken to determine if there was any preferred bonding to carbon or boron atoms in the $1,2\text{-B}_9\text{C}_2\text{H}_{11}$ moiety. The conclusions reached after this study were the following:

- (1) One charge of the $\text{B}_9\text{C}_2\text{H}_{11}^-$ moiety is delocalized in the boron polyhedron in the 5, 6, 9, 10, 11 and 12 positions;
- (2) The 1,2 carbon positions and the 4, 7, 8 boron positions are almost identical in their ability to donate charge;
- (3) The $\pi\text{-C}_5\text{H}_5^-$ and $1,2\text{-B}_9\text{C}_2\text{H}_{11}^-$ ligands appear to be quite similar.

The other major Co-59 NQR study to be examined was done by the Harris and Brown research groups.⁸ The compounds examined had the general formula $\text{MX}_3\text{Co}(\text{CO})_4$. The results of this study are

- (1) When X=phenyl group, the NQR frequencies are lower than for the other substituents; this result was indicative of increased σ -bond order in the M-Co bond for the phenyl substituents;
- (2) The frequencies of all of the trihalo-substituted compounds except $\text{SiCl}_3\text{Co}(\text{CO})_4$ were grouped close together. The lower frequencies for the $\text{SiCl}_3\text{Co}(\text{CO})_4$ compound were judged to be due to the enhanced σ -donor character of the SiCl_3 group.
- (3) For M=Ge, the Co-59 resonance frequencies remained essentially constant through the series. This constancy in the halogermanium series is due to the variation in the Ge-X π -bonding in the order $\text{Cl} > \text{Br} > \text{I}$.

Conclusions:

The need for more work in the area of Co-59 NQR is clearly illustrated by some of the questions and related studies suggested in the literature. For example, Hawthorne and Andrews⁹ reported the synthesis of a neutral compound having the formula $(1,2-B_9C_2H_{11})Co(\pi-C_5H_5)$. Herber indicated that he had obtained the quadrupole coupling constant for the analogous iron compound. It would be interesting to obtain the Co-59 NQR spectrum of the cobalt compound for comparison purposes.

Hartmann et al.,¹⁰ and Wanatabe and Yumagata¹¹ report significantly different Co-59 quadrupole coupling constants for the compound $[CoCl_2en_2]Cl$. It is not clear why such different values were obtained.

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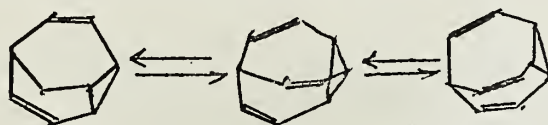
STEREOCHEMICALLY NON-RIGID ORGANOMETALLIC MOLECULES

R. Sneath

November 26, 1968

Introduction

In 1963, Doering and Roth¹ proposed the term "Fluxional Structures" to describe molecules which are distinguished by having more than one geometrically identical potential well. For example, Doering proposed that his invention "Bullvalene" would show only a single resonance in the H' n.m.r. due to the molecule undergoing a series of very rapid cope rearrangements



In 1965, Muetterties² proposed the term "stereochemically non-rigid" as a synonym for fluxional.

σ Cyclopentadienyl Complexes

In 1956, Piper and Wilkinson³ studied a series of cyclopentadienyl organometallic complexes. The IR and UV spectra of several of these compounds indicated that, in some cases, $[(C_5H_5)_2Hg, (C_5H_5)_2Fe(CO)_2]$, a cyclopentadienyl ring was bonded in a σ fashion to the metal. An n.m.r. study of these compounds showed only a single resonance in the H' n.m.r. for the σ cyclopentadienyl protons. Wilkinson proposed that a rapid migration of the metal around the ring was responsible for this proton equivalence.

In 1965, Cotton and Davidson⁴ carried out a crystal structure and low temperature n.m.r. study of $(C_5H_5)_2Fe(CO)_2$ and determined that one of the (C_5H_5) rings was σ bonded to the metal. From this study, they also proposed that the metal migrated by a 1-2 type mechanism around the ring.

Whitesides⁵ later studied the low temperature H' n.m.r. of $(C_5H_5)Cu(PEt_3)$ and proposed that this study indicated that the metal migrated by a 1-3 type mechanism around the C_5H_5 ring.

Cotton⁶ then synthesized and studied the $(\sigma \text{ indenyl})(C_5H_5)Fe(CO)_2$ complex which gave some support to his proposed 1-2 mechanism.

Cyclooctatetrene Complexes

Several cyclooctatetrene complexes have also been observed to show fluxional behavior.

In the study of $(C_8H_8Fe(CO)_3)$, a controversy arose among Cotton, Winstein, and Pettit concerning the structure of this complex in solution. Pettit⁹ and Winstein¹⁰ maintained that it was a 1-3 diene bonded structure, while Cotton¹¹ proposed that it was a 1-5 diene bonded structure.

Cotton's study of $C_8H_8Ru(CO)_3$ in solution^{13,14} showed that the 1-3 diene bonded structure was the most likely for $(C_8H_8)Fe(CO)_3$ in solution.

From this study and one which he carried out on (1,3,5,7 tetramethyl cyclooctatetrene) $Mo(CO)_3$,^{15,16,17} Cotton was able to propose that a 1-2 migration of the metal around the ring was the most reasonable mechanism for the fluxional behavior of C_8H_8 complexes also.

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FLASH HEATING AS A TECHNIQUE FOR HIGH TEMPERATURE SPECTROSCOPY

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I. Introduction

Flash heating is a method for producing a transient thermal effect (maximum duration: a few millisecond) in solid materials by irradiation with capacitor discharge lamps.¹ The temperature rise in the solid should depend upon the incident flux density and the surface area/volume ratio.^{2,3} The helical, xenon-filled flash tubes usually used for these experiments have a peak irradiance as high as 70 KW/cm², compared to 3 KW/cm² for the most intense steady sources, solar and arc image furnaces.⁴ The surface/volume dependence requires that at least one dimension of the sample be less than 100 microns, so that the sample may be in the form of foil, filament or powder, whichever is most convenient.⁵ If the sample is not transparent, the flash will usually cause a phase change or chemical decomposition to give atoms or molecules in the vapor phase. Optical spectra of these species may be recorded with the technique of kinetic absorption spectroscopy.^{6,7,1}

II. Band Spectrum of MnO

MnO is one of the species detected in flash heating and kinetic spectroscopy of KMnO₄.^{8,9} Previous low resolution investigations of the emission spectrum of MnO had yielded conflicting results,^{10,11,12} so we undertook to photograph the spectrum under high resolution and, if possible, make a rotational analysis.

A. Experimental

The emission spectrum of MnO from an air-acetylene flame fed with a solution of MnCl₂ was photographed in the 1st order of the Argonne 30' spectrograph¹³ (plate factor 0.9 Å/mm) and in the 8th, 9th, and 10th orders of a 3.4M Jarrell-Ash Ebert grating (0.5 Å/mm in 10th order). The absorption spectrum of MnO was taken in the 1st order of the 30' spectrograph by the technique of flash heating and kinetic spectroscopy of KMnO₄. 90% O¹⁸ labelled KMnO₄ was used to give the spectrum of MnO¹⁸. Spectra were measured against Th standards on a Tomkins-Fred semi-automatic comparator.¹⁴

B. Results and Discussion

The O¹⁶ - O¹⁸ isotope shift proves that the carrier of the spectrum is MnO and confirms the vibrational analysis. The revised formula for the band heads of MnO¹⁶ is $\nu_{v',v''} = 17941.7 + 756.6(v' + 1/2) - 9.5(v' + 1/2)^2 - 842.9(v'v'' + 1/2) + 5.3(v'' + 1/2)^2$ cm⁻¹. The lower state vibrational constants for MnO¹⁸ are $\omega_e'' = 806.7$ cm⁻¹ and $x_e''\omega_e'' = 5.5$ cm⁻¹. These values agree closely with those predicted by the ratio of reduced masses. The upper state constants could not be calculated because heads were observed for only two vibrational levels.

Despite repeated attempts, no progress could be made with a rotational analysis. Many of the lines are unusually wide owing to blending or possibly hyperfine interaction with the Mn^{55} nucleus. The structure of the spectrum is complicated by extensive perturbations. Our results confirm Gatterer's observation that the 0,0 and 0,1 bands of MnO^{16} are actually headless.¹⁵ The isotope shift moves the perturbation to $v'=1$ in MnO^{18} .

Under high resolution, it can be seen that each band head is made up of 3 or more closely spaced components. No Q heads could be identified, so the transition is a $\Delta\Lambda=0$ type. Since pi states in MnO should show good Hund's case a coupling, the most probable assignment is to $\Sigma-\Sigma$.

It has been shown recently that simple M.O. theory gives a reasonably good explanation of electronic structure in $3d^1$ to $3d^4$ oxides.^{16,17} Some caution is necessary in extending this scheme to MnO because of changes in the relative orbital energies, but the following might well be expected to be low energy configurations:

$3d(\delta^2\pi^*2\sigma^*)$, ${}^6\Sigma$; $3d(\delta^2\pi^*2)$ $4s\sigma^*$, ${}^6\Sigma$; $3d(\delta^2\pi^*)$ $4s\sigma^{*2}$, ${}^4\pi$.

The configuration with the unpaired $4s\sigma$ electron should have a much larger hyperfine splitting,¹⁸ perhaps leading to an increase in line width, as observed in VO .¹⁹

III. Spectra of Excited Atoms: Mn_I and Pb_I

A. Introduction

Flash heating is an excellent method of populating meta-stable excited levels in atoms. Spectra of vapor from flash heated tungsten showed absorption from levels as high as $21,000\text{ cm}^{-1}$ (60 KCal) above the ground state energy levels.²⁰ The population of excited atoms approximately followed a Boltzmann distribution, corresponding to $T = 7200^\circ\text{K}$ at the time of maximum spectral intensity.

B. Mn_I^* in Flash Heating and Kinetic Spectroscopy of $KMnO_4$

(Part of this work was done in collaboration with Dr. Peter Lee.)

Crystals of $KMnO_4$ were flashed at various energies and absorption spectra were taken at different delay times up to 1.5 Msec. All spectra were taken in the 1st and 2nd orders of a 1.5M B and L grating (15 Å/mm in 1st order). The intensity of the Mn_I spectrum increased with increasing radiant energy of the flash, but did not have the same time history as the flash intensity. Absorption from levels at $27,250\text{ cm}^{-1}$ could still be detected more than 1 Msec after the peak flash intensity. Moreover, comparison of the flash spectra to furnace spectra of Mn at 2200°C ²¹ and between the meta-stable levels with those which could decay to ground via an allowed transition showed that the population distribution of Mn^* was non-Boltzmann. It seems likely that the Mn^* is the product of a chemical reaction rather than of thermal excitation.

C. Absorption Spectrum of Pb_{I} $6(^3\text{P}_1, ^3\text{P}_2)$

Lead foil was flash heated in various gases and spectra recorded on a 2M vacuum spectrograph.²² Absorption lines can be seen on the flash spectra which do not appear in furnace absorption²³ or in emission sources.²⁴ Spin-orbit coupling in lead is very large; the lower level, $J=1/2$, in Pb_{II} is $14,000 \text{ cm}^{-1}$ below the upper, $J=3/2$. As a result, 6pns and 6pnd series in Pb_{I} fall into two almost completely separate groups; those which approach the lower limit and those which approach the upper. The $3/2$ members which lie above the $1/2$ limit interact in a very striking manner with the continuum.²⁵ Lines to these levels from $6p^2 \text{ } ^3\text{P}_1, ^3\text{P}_2$ lie in a more easily accessible region, and we have extended the 6pns $^3\text{P}_2^0$ series up to $n=10$, 6pnd $^3\text{P}_2^0$ to $n=8$, and 6pnd $^3\text{F}_3^0$ to $n=8$. Some of the lower members of the $3/2$ series fall among the upper members of the $1/2$ series. Interactions between these $3/2$ levels with $1/2$ levels having the same parity and J value causes interesting perturbations and intensity anomalies. We have discovered a new branch of a $J=2$, 6pnd series from $n=16$ to $n=24$. The intensity passes through a maximum at $n=20$. This series is undoubtedly an extension of $\text{nd } ^3\text{D}_2^0$ or $\text{nd } ^3\text{F}_2^0$, which can be followed up to $n=12$ and $n=13$ respectively, so the unusual intensity behavior is the result of configuration interaction. Garton and Codling observed a similar behavior in the $6\text{snp } ^1\text{P}_1^0$ series in Ba_{I} , which they attributed to interaction with the $5\text{d}8\text{p } ^1\text{P}_1^0$.²⁵ The great puzzle in the Pb_{I} spectrum is the location of levels from the sp^3 configuration.¹ The lowest lying of these should be $^5\text{S}_2^0$,²³ which may in fact be the level interacting with the nd series.

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BIO-INORGANIC SYSTEMS: THE DETERMINATION OF THE CHEMICAL AND STRUCTURAL PROPERTIES OF HEMOGLOBIN

James S. Swanson

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Introduction

By the turn of the century the importance of metalloporphyrin complexes in biological systems had been well authenticated. This was due mainly to the work of Felix Hoppe-Seyler¹ with the hemoglobins and Willstätter and Stoll with chlorophyll.

The hemoglobins are stable conjugated proteins. It has been shown by chemical means that they all contain the same prosthetic group,² a protoporphyrin Fe(II) complex (protoheme), and that this group can be separated by mild acid hydrolysis.³ It follows that the variations in physiological function are governed by the protein moiety. The structure and properties of protoheme were determined largely by the work of Fisher and Küster culminating in the complete synthesis of protoheme.⁴ The story of hemoglobin, its chemical, structural, and physiological properties has been unfolding for over 150 years and includes in its repertoire contributions from such famous names as Michael Faraday (magnetic studies), C. Bohr (Bohr Effect), and Linus Pauling.

Although hemoglobin is an inorganic complex, its study has been separated into a completely organic and a separate inorganic aspect, with the two parts being worked on independently.

Chemical Studies

It was recognized early in the twentieth century that the hemoglobins were the oxygen-carrying proteins of the vertebrates. The first chemical studies were therefore aimed at elucidating the nature of the chemical bonding in these substances, with the hope of explaining their known physiological functions.

In 1904 Bohr⁵ studied the effect of varying the partial pressure of CO₂ on oxygenation of native hemoglobin. This was soon correlated with changes in the acid strength of hemoglobin upon oxygenation and has become known as the Bohr effect.

In 1936 Pauling and Coryell⁷ studied the magnetic properties of native hemoglobin, oxygenated hemoglobin, and carbonmonoxy-hemoglobin. On the basis of these studies, Pauling suggested that the bonding in the latter two metal porphyrin complex is covalent.

Wyman⁸ made an extensive thermodynamic investigation of the oxygenation of hemoglobin in 1938. He found a discrepancy between the calculated and observed heat of oxygenation which corresponded almost exactly to the heat of dissociation of histidine and postulated that iron was coordinated to two histidine residues in the globin chain, as well as to the protoheme. His resultant model also accommodated the Bohr effect quite well. A further hypothesis regarding the Bohr effect and histidine-iron interactions was expounded by Pauling and Coryell in 1940.⁹

At about this time, the first chemical evidence supporting the existence of molecular diseases emerged from the studies of Pauling et al.¹⁰ on hemoglobin S, an abnormal form of hemoglobin associated with sickle cell anemia.

The chemical investigations of hemoglobin culminated with the complete elucidation of the amino acid residue sequence in the various globin chains of most of the normal and abnormal hemoglobins.^{11, 14}

Structural Studies

By 1935 the power of X-ray diffraction as a tool in the precise determination of three dimensional molecular structures was becoming apparent. In 1938 a group of Cambridge crystallographers began the X-ray diffraction studies of hemoglobin.¹² A number of other investigators also took up this problem, but the structural solution eluded all attempts for a period of twenty-five years. The problem was finally solved by the technique of isomorphous substitution.¹³ The results of the structural investigations have supported most of the previous conclusions reached by purely chemical means including the sequence of amino acid residues, the histidine interactions with the protoheme, and the explanations for physiological activity.

Some Physiological Implications

It is known from the magnetic⁷ and spectroscopic studies⁶ that the iron in hemoglobin is maintained in the +2 oxidation state. This fact is largely responsible for the easily reversible coordination to oxygen. The stabilization of complexation and the +2 oxidation state is known to be strongly pH dependent (Bohr Effect).^{5, 8, 9} Pauling has shown how coordinated histidine shifts its acidity (by resonance) to stabilize either the oxygenated or deoxygenated protoheme.⁹ In the severe forms of anemia, it is known¹⁴ that the iron is not stabilized in the +2 state, but is oxidized to the +3 state where it forms a stable oxygen complex. Structural and chemical investigations of hemoglobin M¹⁴ have shown that in this abnormal molecule the coordinated histidine is replaced by another amino acid residue (either tyrosine or glutamic acid) which is not capable of stabilizing the +2 state. Other studies have indicated that there is at least one amino acid residue, arginine, which can replace the histidine and not destroy the activity of hemoglobin. However, persons having this defect become severely anemic when treated with sulfa drugs.¹⁵ Presumably, reactive moieties on the sulfa drugs render arginine incapable of stabilizing the +2 state of iron.

Inorganic Applications

The hemoglobin case may be taken as a profound example of what can be accomplished through the fusion of inorganic and bio-organic chemistry in elucidating a physiological problem. In recent years, a considerable quantity of empirical data for biologically related inorganic complexes has been amassed.¹⁶ The synthesis of this information into a more utilitarian form is the aim of much current research and thought in this field.

For example, one of the most challenging tasks undertaken in the hemoglobin studies was the determination of the amino acid sequence in various globin chains. This problem was solved by the development of new and improved techniques of organic separations. It may have been solved by the application of inorganic methods, as indicated by the following results. Divalent transition metal cations are known to catalyze the hydrolysis of peptides.¹⁷ Recently, Collman and Buckingham¹⁸ have demonstrated the hydrolytic cleavage of N-terminal peptide bonds using cis-hydroxyaquotriethylene-tetraminecobalt (III). This reaction occurs under relatively mild conditions (pH 7-8, 65° C) and forms an amino acid complex which may be isolated by column chromatography, and identified by standard inorganic techniques.

A further sophistication would be the development of thin layer chromatographic techniques for the separation and identification of inorganic complexes. At least one such study has been reported in the recent literature.¹⁹

Conclusions

Many of the physicochemical problems under current investigation are known to involve inorganic complexes. The approach to these problems has been primarily organic. It is suggested that a predominantly inorganic approach may yield faster and more complete results.

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PHOTOCHEMISTRY OF Cr(III) AND Co(III) INORGANIC COMPLEXES^{1,2,3}

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Introduction

The photosensitivity of coordination compounds has been known since the earliest literature in the field of inorganic chemistry. With the advent of fluorescent lighting, this subject has rapidly expanded from qualitative to quantitative investigations in applications to preparative chemistry and thermal kinetics. Now, inorganic photochemistry is established not only independently, but also with some inter-relations with organic chemistry.

In this seminar, only the photochemistry of inorganic coordination compounds of Cr(III) and Co(III) will be discussed. In addition, primary photochemical processes will be considered, and little attention will be given to subsequent reactions of radicals or other molecular fragments.

Electronic States of Coordination Compounds

Crystal-field excited states typically involve promotion of a d electron from an orbital directed away from the ligand position to one directed toward them. Individual electronic configurations are described by spectroscopic terms. Transitions between states of the same parity are Laporte forbidden and changes in multiplicity are spin forbidden.

The second type of absorption band with higher energy and larger extinction coefficient are charge transfer bands. These are of two basic types; those in which electron density has moved toward the central atom [CTTM] and those in which electron density has moved outward [CTTL or CTTS].

Excited-States Processes

The excited state may be in a high vibrational state as evidenced by the broadness of the absorption and emission bands and the red shift of the latter relative to the former. The explanation is that the transition obeys the Frank-Condon principle.⁴ The high vibrational level of the excited states indicates that the zero vibrational level has a geometry different from that of the ground state.^{4,5}

Thermal equilibration of the excited state to zero vibrational level by energy exchange with the medium is achieved very rapidly. The equilibrated excited state may return to the ground state by emission or by radiationless deactivation.⁶ Emission and radiationless deactivation to the ground state may be hindered in the case of complexes and internal conversion is considered to be very fast.⁴ Therefore, excited states are usually followed by a rapid deactivation to the lowest excited state of the same multiplicity.⁵

The excited states may also undergo a radiationless transition to a state of different multiplicity, i.e., intersystem crossing.⁶

Finally, an excited state may lead a chemical reaction.

Photochemistry of Cr(III) Complexes

With a few possible exceptions of shorter wavelength, photolysis always consists of substitution or substitution related reactions uncomplicated by redox processes, and the quantum yields are generally high. It is very convenient to consider first those complexes having Oh symmetry. Since only one kind of ligand is present, only one kind of substitution reaction is possible. Therefore, the wavelength and temperature dependence of quantum yield can be determined.

The spectra of Cr(III) complexes are understood theoretically in some detail.⁷ Cr(III) complexes typically show at least two quartet-quartet transitions and one spin forbidden transition.⁸ The 2E_g spin forbidden excited state involves only spin pairing within a non-bonding set of orbitals, so that the transition is relatively insensitive to the type of ligand⁹ and the bond is structured, indicative of vibronic coupling.⁸

The phosphorescent emission of 2E_g is only slightly shifted in position from that of the absorption band, but ${}^4T_{2g}$ state is broad and red shifted.^{10,11} The reason is that ${}^4T_{2g}$ state is strongly distorted, possibly to another point group.^{5,12}

Studies of the photochemical process of Cr(III) for Oh symmetry has been systems involving aquation. The aquation quantum yields are high and increase with increasing ligand field strength. They are wavelength and nearly temperature independent.

Some non-Oh symmetry complexes have been studied [D_{4h} or C_{4v}]. Quantum yields vary from one to 10^{-4} . They are more often wavelength and temperature dependent. There are three empirical rules for low-symmetry complexes.⁵

1. Six ligands lie in pairs at the ends of three mutually perpendicular axes. That axis having the smallest average crystal field will be the one labilized.
2. If the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates.
3. The discrimination implied by rule 1 and 2 will occur to a greater extent if first quartet-quartet transition is irradiated.

The chemical reaction may occur with the molecule in any excited state, but this state should contain sufficient energy, be of long life, have an electronic configuration which makes it possible substitutionally labile, and have a zero crystal field activation energy for reaction. One proposal suggests that reactions occur in the 2E_g state,¹³ however, there is no increasing in quantum yield on irradiation of the 2E_g region.¹⁴ A more recent proposal is that reaction may occur with the molecule in the ${}^4T_{2g}$ state.⁵ The equilibrium excited state has sufficiently different geometry from that of the ground state, so that deactivation is hindered. The photolysis rule 1 could be explained since according to ligand field theory, the ${}^4T_{2g}$ state is obtained by promoting an electron into an antibonding orbital along the z or weak field axis.

A rather different proposal is that the reacting species may be a vibrationally excited or hot ground-state molecule,¹⁵ but this species should react like the ordinary activated molecule of thermal kinetics, implying that the photochemical process should be the same as the thermal one. Such a mechanism has been discounted by the different results of photochemistry and thermal chemistry.

Along a different line of thought, it is suggested that cage reactions are the basis of molecules in photochemistry. That is, the reactions involved must be brought into contact by a diffusion process when the quantum of radiation is absorbed.¹⁶ But diffusion is temperature dependent and quantum yields of Cr(III) complexes are not.

From the above discussions, it is concluded that the $^4T_{2g}$ state is the most acceptable.

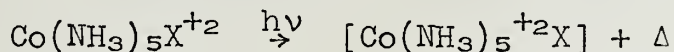
Photochemistry of Cobalt(III) Complexes

When Co(III) and Cr(III) photochemistry are compared, we find that Cr(III) photochemistry is substitutional, but that of Co(III) is of the photoredox reaction type. This major difference is responsible for the much longer wavelength position of first CT band in Co(III) complexes as compared to Cr(III) complexes. It is found that Cr(III) complexes are, in general, stable to thermal redox reaction, both kinetically and thermodynamically, whereas Co(III) ones are not.

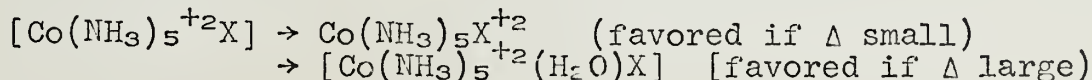
Radiation of about 370 mμ is used for $Co(NH_3)_5X^{+2}$ complexes. No redox reaction occurs with $X = NH_3, SO_4, Cl$. With $X = Br, NO_2, NCS, N_3$ and I , photoredox reaction gives quantum yields from 50% to 100% respectively. This sequence coincides with the movement of the CT band into the d-d transition.¹⁷ It is clear that the CT excited state is responsible for the redox process [CTTM type]. Irradiation of the d-d transition leads to aquation and the quantum yield is less than 10^{-3} . From the above results, we find first, that the ligand field excited states photoaquate in low quantum yield, and that CT excited states undergo redox reaction in high quantum yield. Secondly, the aquation quantum yield can be made fairly high on irradiation of a CT bond.¹⁸

The generalization has been made that CT excited states lead to redox reaction and ligand field ones lead to substitution. But, in the case of Co(III) complexes, the ligand field excited states seem to be only slightly photoactive, and the large aquation quantum yields observed in those cases where low-lying CT bands are irradiated need further explanation.

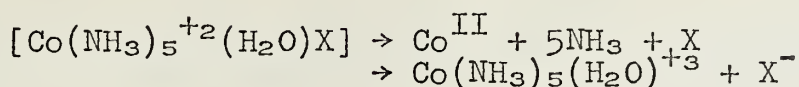
The primary process is considered to be homolytic bond fission, and in terms of an acidopentaamine, the process is^{19,20}



where Δ represent excess energy. Cage reactions then follow, in which X can be reassociated or can begin to diffuse away



Final escape of X leads to a net redox decomposition, but X might regain an electron without itself being able to recoordinate, so that aquation would result



The above mechanism accounts for high aquation yields of Co(III) complexes on irradiation of CT bands. However, this mechanism does not hold at a wavelength much longer than that of the first CT band.²¹ As a further comment, the fact that the cage reaction mechanism would be largely diffusion controlled perhaps accounts for the apparently generally small temperature coefficients of quantum yields for Co(III) complexes.^{18,22}

The lower quantum yields of d-d transition of Co(III) complex can be due slower chemical reaction and faster deactivation, relative to Cr(III) complexes. The first assumption can be accounted for on the basis that in Cr(III) excited states a t_{2g} orbital is free for additional bonding by an entering group, while this is not the case with Co(III).

It has also been suggested that singlet-singlet radiationless deactivations may be inherently very fast.²¹ The Co(III) in the first excited state is more likely to retain the same geometry as the ground state, so that deactivation could be very fast. There is no potentially long-life excited state in Co(III) complexes.

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